In-situ optical thickness & easy packing density measurements as novel approach to development of OLED

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Abstract

Optical thickness method using double interferometer showed dynamic variations of both mechanical and optical thicknesses. Packing density measured a thickness ratio of before and after pressed single film. Lower swelled thickness of emitting layer in a device and densely packed film had shown better lifetime.

1. Introduction

Since discovering organic light emitting diode(OLED), it has been making arduous efforts to pave the way to realize an application of display for a long time. In the mean time, a lot of analysis method of an organic film keep track of the developing history of OLED's performance like color, efficiency and lifetime.

But, most of the analyzing tools had been invented and improved to investigate an atomic position and identify the elements in the device or film made of semiconducting inorganics and metals. For that reasons, according to uncertainty principle, it requires higher photonic and electronic energy. Thus, if you want to apply such tools to study organic system mostly consisted of carbon, hydrogen, nitrogen and oxygen you should have to struggle against the principle due to their lightness, low binding energy and even lower interaction between molecules. The problem also basically occurs even during preparing samples for analysis, i.e. making clear surface or cleavage. If you were interested in only surface, then, your research would be limited to single films or top surface of multi-layered devices.

Considering above, OLED is a multi-layered organic device. Thus, we have two natural handicaps, which might have been working as drawbacks to decelerate the OLED development. To make matters worse, benzene-based conducting organic materials have countless designed molecular structures as single molecule, dendrimer and polymer, which fact, I think, also make the speed down. In our experience, polymer system could endure high energy of probing photon and electron, showing better contrasting images and component information. But, it's not enough to fulfill our desire of understanding failure/degradation mechanism and developing further performance to meet specifications of display.

In this study, we propose optical thickness and packing density measurements as new analyzing methods. Optical thickness is to measure thickness variation of emitting layer during operation by a way of interference mechanism [1]. It could give us dynamic information of OLED. Generally, organic conducting material has very low conductivity like having almost insulating property. When we drive, i.e., apply current into the device it generates joule heating within device, especially, emitting layer to increase total thickness, which organic layers are penetrated and reflected on metal by coherent photon from laser to make interference pattern with other bypassed one. On the contrary, packing density is to measure penetrated depth of stylus depending on applying stylus force. It could give us static information of single and multi-layered films.

2. Experimental

We There was a report of G. Dennler to measure electromechanical strain by using Nomarsky interferometer for the application of PLED to actuator [1]. We modified measuring scheme using double interferometer shown in Fig.1(a). He-Ne laser beam (632.8nm) was divided into two paths by beam splitter (BS). One path named by "A" went through transparent encapsulation glass to be reflected back at metal side. The other one named by "B" went through

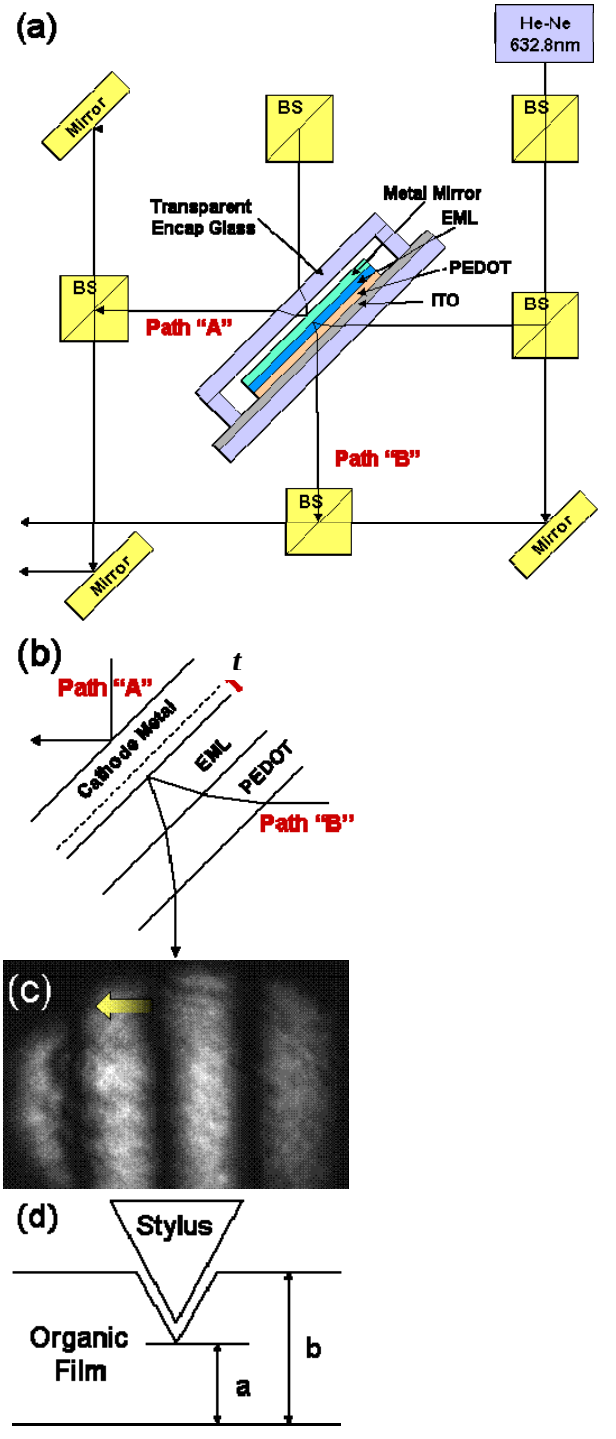


Fig.1. (a) Schematic diagram of "Optical Thickness" measurement system where BS=beam splitter, (b) Detailed beam path passing by two ways of both metal side(path "A") and glass side(path "B") and thickness variation, *d*, (c) Interfering pattern monitored with CCD camera and the direction of pattern movement when operating OLED, (d) Schematic diagram of "Packing Density" measurement system.

substrate glass, where the light feels the change of both physical thickness and refractive index of emitting layer (EML) due to lowering density, which could be seen in detail in Fig.1(b). Thus, we just call it as optical thickness [2]. Such two interfered paths measured as stripe patterns were monitored simultaneously with CCD camera. The pattern in Fig.1(c) was fitted by sinusoidal curve to obtain peak movement during the device turns on and off. But, firstly, we should know the meaning of direction. For example, left movement means increase of optical thickness.

Packing density is one way of measuring how the film is condensed after deposited or spin-casted. We can usually obtain that by using ellipsometer. But, we are also able to measure that in very simple way with alpha-step profiler varying the force of stylus having a tip area of $1\mu m^2$. From Fig.1(d), packing density could obtain as a ratio of a/b called relative thickness. Then, the higher a/b represents the denser film formed.

In order to apply above analysis tools to OLED, we prepared samples of polymer and small molecular EL devices. And, in case of polymer, we used several blue emitting materials like TS9, NTS9, B9 synthesized by Dr. Son and Park to verify such tools as new analyzing methods.

3. Results and discussion

The optical thickness (OT) is defined from

$$\sum_i \frac{4\pi}{\lambda} d_i n_i(\lambda) - \varphi_{top}(0,\lambda) - \varphi_{bottom}(0,\lambda) = 2m\pi \quad [2] \qquad (1).$$

Then, if we differentiate both sides we can obtain

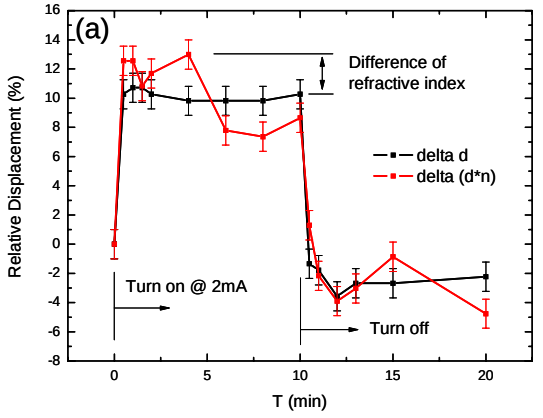
$$\frac{2\Delta(d \cdot n)}{\lambda} = \Delta m \qquad (2),$$

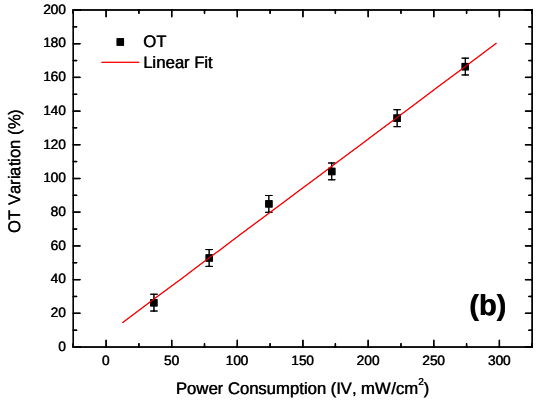
where d is a length of light, n refractive index, λ wavelength, and m number of fringes. If we consider the geometrical situation of measurement system shown in Fig.1(b) we can make a relation with (2) like

$$\Delta d = \frac{2\Delta t}{\sqrt{1-(n^{-1}\sin\theta_i)^2}} \qquad (3),$$

where t is a thickness of EML and θ_i incident angle (45°).

We applied constant current (2mA) as doing in lifetime measurement for some time (10mins) and turned off by several periods shown in Fig. 2(a) with both mechanical (Δd) and optical thicknesses ($\Delta(d \cdot n)$). The difference between them represents the variation of refractive index of emitting layer due to electromechanical strain. In this case, considering





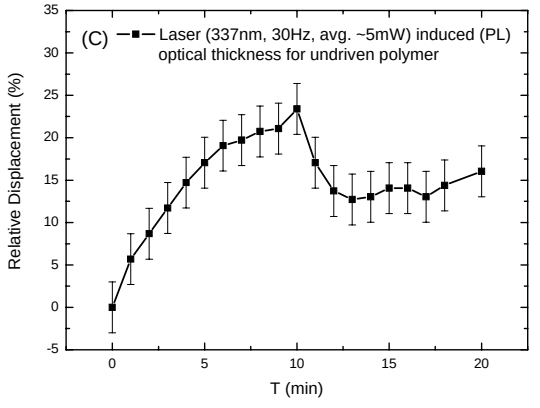


Fig.2. (a) Comparison of path "A" as Δd and path "B" as Δ(d·n), showing difference due to the variation of refractive index of emitting layer, (b) Dependence of optical thickness(OT) according to driving power, (c) OT results measured with applying pulsed UV layer (337nm, ~5mW) rather electrical voltage.

equation (2) and (3), relative displacement (Δ*m*) of ~10% corresponds to thickness increase by ~11nm, i.e., 14% of total thickness of emitting layer, 80nm at 2mA, emitting ~16000cd/m^2. Then, for normal operation with ~1000cd/m^2, emitting layer would swell by few Å, which fact could be proved from the results in Fig.2(b), showing clear linearity between power consumption vs. optical thickness variation.

It is interesting to know that, for bipolar and hole-only polymer devices, OT in the bipolar device relatively varies by 20~30% larger than that of the hole-only device. It means that light emitting recombination zone consumes more power. Even more interesting result is shown in Fig.2(c). We applied high powered pulsed layer into OLED for 10mins rather than electrical filed. Then, it also showed similar behavior of optical thickness variation. Therefore, from above results, it is enough to make us imagine what happens inside OLED during operation.

We measured both optical thickness and packing density for three kinds of polymer, TS9, NTS9, B9 shown in Fig.3, where TS9 consisted of spiro-fluorene and phenoxazine moieties with ratio of 9 to 1, NTS9 had an modified phenoxazine moiety, and B9 had a butterfly-fluorene moiety instead of spiro-fluorene. By increasing probe(stylus) force, B9 shows better packing density comparing to others. Since the portion of phenoxazine moiety is 10% and modification has been done partially there's not much change of packing density. But, change of major moiety results a quite different value shown in Fig. 3(a). In a dynamic point of view in polymer device, results of Fig. 3(b) also show consistent tendency. Relatively, B9 shows much less variation of optical thickness than that of others. But, in case of NTS9 having little modification of phenoxazine moiety, the values locates almost in the middle of TS9 and B9. It means that the little modification was not obviously shown in static state, but, in dynamic state, it had a clear effect. The difference of mechanical and optical thicknesses is higher in B9 than TS9, which fact represents that, in denser film, relative change of refractive index has more influence. With summarizing above results, we could understand the luminance and voltage curves shown in Fig. 4. Here, the voltage variation corresponds to change of internal resistance because the device was driven by constant current. TS9 always shows faster luminance drop at around 120 hrs in higher luminance level (65%), which is called as a tail drop. At the same time, resistance grows rapidly. Even though there's no much difference of lifetime with TS9, NTS9 shows less tail drop, but, has early starting

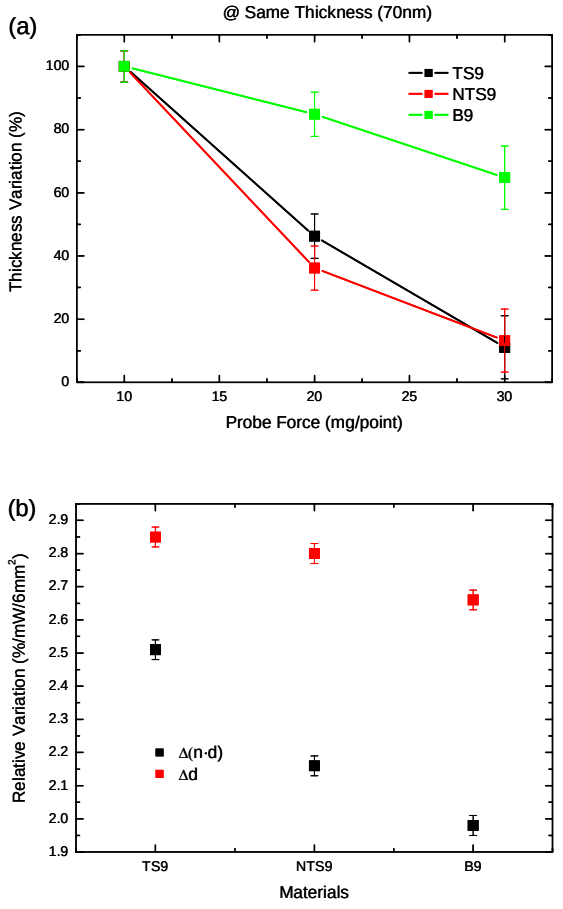


Fig.3. (a) Dependency of packing density for stylus force, (b) Results of both thickness and optical thickness per unit power and emitting area.

at around 60 hrs. Interestingly, the resistance slope after start of tail drop shows almost a linear behavior, indicating slower degradation of emitting material. For B9, the situation is quite different. Basically, the resistance slope is much low, i.e., material degradation occurs slowly. Thus, during the luminance drops down to 50%, there's no a tail drop happened, resulting a much improved lifetime.

In our study, we did apply the optical thickness and packing density mostly into polymer devices, which shows bulk degradation behavior like generation of insoluble layer near anode side [3]. We believe as shortly shown in Fig. 4 that such novel analyzing methods could apply to small molecular devices, where degradation usually occurs at the interface between two different organic layers. Thus, it will help us screen best material and develop most wanted device as further works.

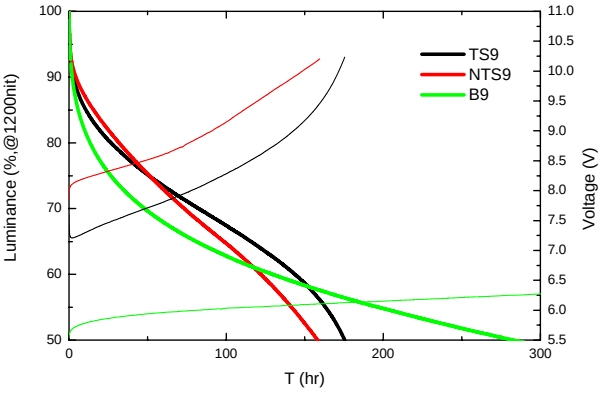


Fig.4. Life curves of different materials, showing luminance drop (thick line) and driving voltage (thin line) in constant current mode.

4. Summary

As novel investigating methods for OLED, the optical thickness and packing density measurements had been invented and had applied to mostly polymer. Basically, organics materials change their thickness, i.e., packing status for applying electric field and photons. The nature becomes to vary while operating with growing degradation of material. The optical thickness could give us time-dependent information of the nature. On the contrary, packing density just measures static feature of a film. In relations with the results of optical thickness, we can presume the degradation mechanism and establish some guide line to predict materials showing longer lifetime at least in polymer device. We expect further improvement in small molecular case as well.

5. References

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