

Effect of Duty Ratio of Driving Voltage on the Forming Process in Aging of Organic Electroluminescent Device*¹

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An interesting phenomenon “forming process”, namely, the rising process of luminance and efficiency at the initial aging of organic electroluminescent devices, was studied under constant pulse voltage excitation with different duty ratios. The device has a conventional double-layer structure. Tris(8-quinolinolato) aluminum (Alq) was used as the emitter layer, and poly(N-vinylcarbazole) (PVK) was used as the hole transport layer (HTL). The increase of luminance is due to that of the current. It was assumed that the forming process results from the redistribution of the electric field in the organic layer due to the build up of space charge at the interfaces as well as other factors.

KEYWORDS: forming process, aging, organic electroluminescence, rising process, decaying process

1. Introduction

Since efficient organic electroluminescence (EL) was first reported by Tang and VanSlyke in 1987,¹⁾ organic EL has attracted much interest because of its attractive properties such as high luminance, low driving voltage, easy fabrication of a large area and a wide range of emission colors.^{2–6)} From a practical point of view, an important aspect is to prolong the lifetime of the devices. For this purpose, some significant achievements have been made. It was shown that the EL device with a structure consisting of double hole-transport layers exhibits significant operation stability.⁷⁾ The lifetime of encapsulated devices can be greatly increased as compared with that of unencapsulated ones.⁸⁾ The formation of a small energy barrier at the interface of the hole transport material/anode was demonstrated to be required for high durability.⁹⁾

Studies on the aging process of the organic EL devices showed that the devices have a limited lifetime in an ambient atmosphere. When operated at a constant drive current, luminance and efficiency usually decay gradually from a rapid rate to a slow rate, accompanied by an increase in drive voltage, which indicates that the resistance of the device increases during the aging process.^{8,10,11)} Recently, a forming process was found in the aging of a highly stable organic EL device with a multilayered thin-film structure and an ac drive waveform,¹²⁾ that is, the luminance and efficiency of the device increase at the initial step of aging. A similar phenomenon was found in the device under DC pulse voltage.¹³⁾ The existence of the forming process indicates that the aging process is a very complicated process. The study on the forming process is undoubtedly helpful to understand the mechanism of aging and will provide a new route to improve the characteristic of luminance decay. In this letter, we concentrate on the effect of pulse voltage with different duty ratios on the forming process, and the differences between the forming processes of organic EL and direct current EL (DCEL).

2. Experimental

Figure 1 shows the organic EL device structure and the

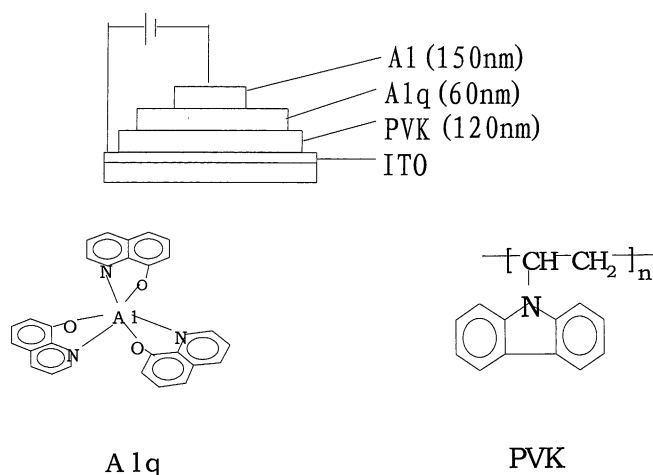


Fig. 1. Organic EL device structure and the molecular structures of the materials used in this study.

molecular structures of the materials used in this study. The organic EL devices had a conventional double-layered structure. We use poly(N-vinylcarbazole) (PVK) as the hole transport layer (HTL) and tris(8-quinolinolato) aluminum (Alq) as the emitter layer (EML). The PVK films were formed by spin coating from a chloroform solution onto a glass substrate coated with indium tin oxide (ITO), and then an Alq layer and Al contact were deposited successively on top of the PVK film by vacuum deposition in a high vacuum of 5×10^{-5} Torr. The deposition rates for the Alq layer and Al contact were about 0.4 nm/s and 2 nm/s, respectively. The stability tests were performed in an ambient air, at a constant voltage of 10 V. The light output and the forward bias current were monitored continuously throughout the stability test. The luminance was measured with a luminance meter, ST-86LA, while simultaneously measuring the current with a multimeter serially connected with the driving circuit. The power was supplied by us, which can output constant pulse voltage with various duty ratios.

3. Results and Discussion

Table I shows the aging data of the same kind of devices under constant pulse voltage of 10 V with different duty ratios. The aging properties of the devices are illustrated in Fig. 2.

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Table I. Aging data of the devices under different driving conditions

Device	Duty ratio of the voltage applied	The initial luminance (cd/m ²)	The initial current density (mA/cm ²)	The initial luminous efficiency (lm/w)	The real time of the forming process (S)
A	100%	34	10.4	0.108	10
B	50%	15	7.1	0.065	10
C	20%	6	4.2	0.045	11

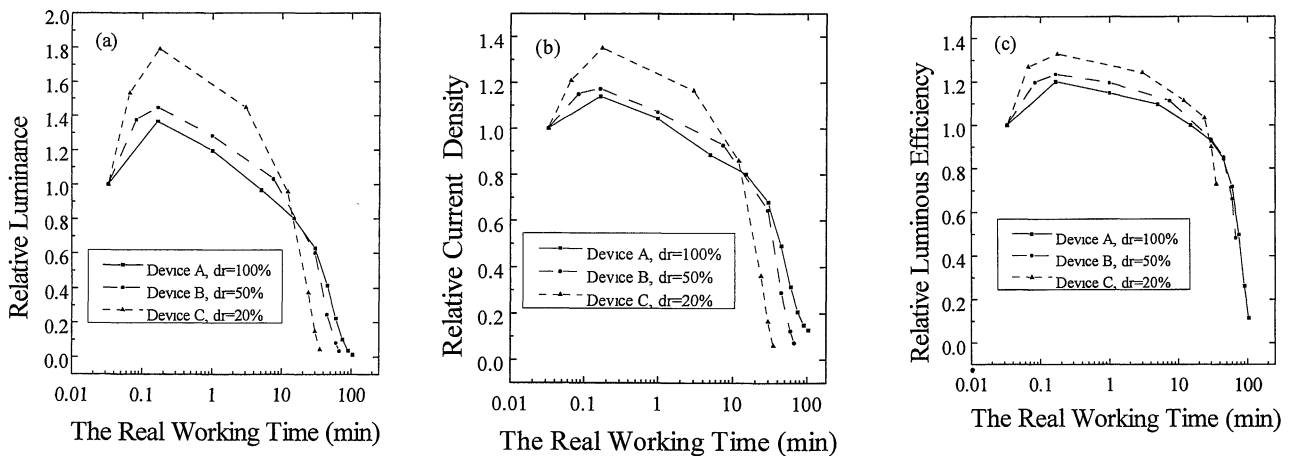


Fig. 2. The aging properties of the EL devices applied with 10 V pulse voltage with different duty ratios (dr): (a) aging of relative luminance, (b) aging of relative current density, (c) aging of relative luminous efficiency.

Table I shows that the initial value of each device is quite different. When the constant voltage with a lower duty ratio is applied to the device, it shows a lower initial luminance and current due to the shorter real working time and integrated measurement. Figure 2 shows that there exists an interesting characteristic of the forming process during the aging in all the devices. Namely, the luminance, current and efficiency of each device go up first before decaying under constant voltage. Concerning one device, the aging property of luminance is very similar to that of current, but the relative intensity of luminance increases more than that of current in the forming process, and the decay rate of luminance is also larger than that of current. The rate of change of luminance is larger than that of current, implying that there is a nonlinear relationship between luminance and current. The luminous efficiency determined by the luminance and current density increases at the forming process.

Figure 2 also illustrates that under constant pulse voltage, the decrease of the duty ratio leads to a large range of the increase in luminance, current and efficiency of the devices. The maximum increase of luminance, current and efficiency in the forming process is achieved when the pulse voltage with lowest duty ratio is applied to device C. Since device C was influenced by the Joule heat less than the others, it is assumed that the forming process and the decaying process are probably competitive processes. Although the operating times of forming processes of the devices A, B and C change markedly at different duty ratios, which are 10, 19 and 53 s, respectively, the real time of the forming process changes little.

In order to understand the forming process of organic EL,

we should compare the forming processes of DCEL and organic EL. Forming process is once the characteristic phenomenon of the film or powder DCEL.^{14,15} The typical character of DCEL shows that when a high dc voltage is applied to an EL panel, a large current flows at first and then the current drops markedly, associated with the onset of light emission. After some time, the current settles down to a constant value and the luminous efficiency of the EL panel rises to a higher level.¹⁴ In DCEL, the forming process is one of the most critical factors in the preparation of the cell; light is only emitted from the device after the occurrence of a forming process, which occurs irreversibly only once in the panel lifetime.¹⁶ There are some differences between the forming processes of DCEL and organic EL. The changes in luminance, current density and efficiency of DCEL are not synchronized. However, in organic EL, the variations of luminance rising and decaying tend to that of current, and the efficiency changes synchronously, which are clearly shown in Fig. 2. It was found that the forming process in organic EL can occur many times by interrupting the operation during the stability test and then restarting it. Therefore during the forming process, the changing of the organic materials would appear to be unlikely.

It is well known that the organic EL device is a charge-injection-type device in which light is generated from the recombination of holes and electrons injected from electrodes. The luminance is mainly determined by the current density injected into organic EL devices. It should be noted that the aging property of luminance is closely similar to that of the current density of each device under different duty ratios, so the rise in luminance in the forming process can be attributed to the rise in current. The increase in current density indicates

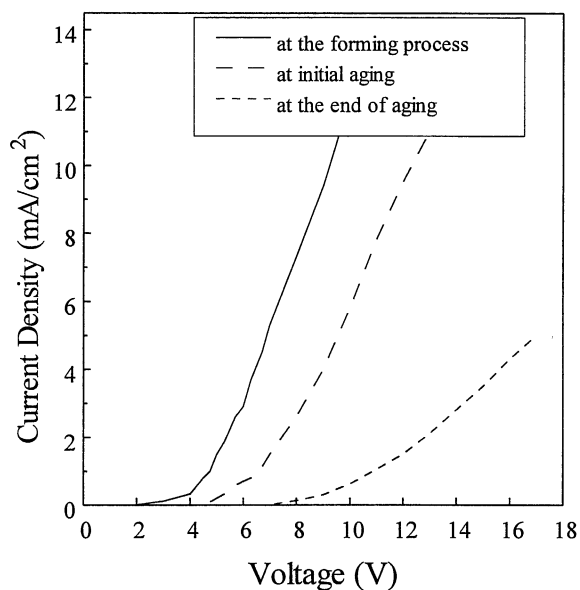


Fig. 3. I - V characteristics of the device.

that the resistance of the device decreases. In our device, the total resistance consists of the serial resistances of the PVK layer, the Alq layer, the contact between the two organic layers, and the contacts between the electrodes and the organic layers. Considering the fact that PVK and Alq are very stable materials, it can be assumed that the contact resistance is most likely to change. Figure 3 shows the I - V characteristic of the device. Compared with the initial one, the injection current density increases during the forming process, and decreases during the decaying process. This result indicates that the efficiency of the injection current increases in the forming process and decreases in the decaying process.

We assumed the mechanism of the forming process to be as follows. It was thought that the different barriers of electron or hole at the heterojunction and between the electrode and the organic layer that made contact with it, would inevitably result in the charge confinement and accumulation at the heterojunction, which would further lead to the redistribution of the internal electric fields within the device and the improvement of injection efficiency.¹⁷⁾ In our device, we consider that there is an accumulation of the carriers at the contact between the two organic layers, and at the contacts between the electrodes and the organic layers. These factors can increase the injection current density and the balance injection of the electron and hole, so as to result in the rise of luminance and cur-

rent density. But the rise of current density will speed up the decaying process of the device, so that it shows the forming process over a limited time. As a result of the weaker influence of the Joule heat, the decrease in duty ratio will lead to a more obvious forming process. A little change in the real time of the forming process for the three devices is possibly due to the difference in influences of oxygen and moisture in the air on the three devices. It needs to be tested if effective encapsulation methods can improve the time of the forming process.

It is assumed that there are other factors resulting in the forming process. For instance, there may be ion conductance by the electric field in the organic EL due to the impurity of the materials. The ions accumulated at the electrode may lower the barrier between the organic layer and electrode, so as to increase the injection efficiency of carriers.¹⁸⁾ It should be noted that the EL efficiency increases during the forming process, therefore the investigation on the forming process may reveal a useful method of improving the characteristic of the devices.

- 1) C. W. Tang and S. A. VanSlyke: Appl. Phys. Lett. **51** (1987) 913.
- 2) C. W. Tang, S. A. Vanslyke and C. H. Chen: J. Appl. Phys. **65** (1989) 3610.
- 3) C. Adachi, S. Tokito, T. Tsutsui and S. Saito: Jpn. J. Appl. Phys. **27** (1988) L269.
- 4) C. Adachi, T. Tsutsui and S. Saito: Appl. Phys. Lett. **57** (1990) 531.
- 5) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns and A. B. Holmes: Nature **347** (1990) 539.
- 6) D. Braun and A. J. Heeger: Appl. Phys. Lett. **58** (1991) 1982.
- 7) Y. Shirota, Y. Kuwabara, H. Inada, T. Wakimoto, H. Nakada, Y. Yonemoto, S. Kawami and K. Imai: Appl. Phys. Lett. **65** (1994) 807.
- 8) P. E. Burrows, V. Bulovic, S. R. Forrest, L. S. Sapochak, D. M. McCarty and M. E. Thompson: Appl. Phys. Lett. **65** (1994) 2922.
- 9) C. Adachi, K. Nagai and N. Tamoto: Appl. Phys. Lett. **66** (1995) 2679.
- 10) Y. Hamada, C. Adachi, T. Tsutsui and S. Saito: Jpn. J. Appl. Phys. **31** (1992) 1812.
- 11) H. Tokailin, M. Matsuura, H. Higashi, C. Hosokawa and T. Kusumoto: Proc. SPIE **1910** (1993) 39.
- 12) S. A. Vanslyke, C. H. Chen and C. W. Tang: Appl. Phys. Lett. **69** (1996) 2160.
- 13) X. Liu, W. Li, J. Yu, Y. Zhao, X. Zhao, Y. Yu, G. Sun and G. Zhong: Chin. J. Lumin. **17** (1996) 376.
- 14) H. Kwarada and N. Ohshima: Proc. IEEE **61** (1973) 907.
- 15) A. Vecht: J. Lumin. **7** (1973) 213.
- 16) A. Vecht, N. J. Werring, R. Ellis and P. J. F. Smith: J. Phys. D **2** (1969) 953.
- 17) A. R. Brown, D. D. C. Bradley, J. H. Burroughes, R. H. Friend, N. C. Greenham, P. L. Burn, A. B. Holmes and A. Kraft: Appl. Phys. Lett. **61** (1992) 2793.
- 18) Q. Pei, G. Yu, C. Zhang, Y. Yang and A. J. Heeger: Science **269** (1995) 1086.