Device degradation and the circular polarization of the electro-phosphorescent organic light-emitting diode with a ferromagnetic cathode

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Abstract. Circular polarization of organic light-emitting diode with a ferromagnetic metal Fe cathode and with a phosphorescent molecule Ir(ppy)$_3$ was observed. The maximum degree of circular polarization was 0.4 % at constant voltage operation and 0.6 % at constant current operation. Degree of circular polarization was independent of device degradation process. Both the maximum degrees of circular polarization were much smaller than the value expected from the spin-polarization at Fermi energy of the Fe cathode. Efficient spin-injection and spin-transport into emissive molecules are expected to improve the degree of circular polarization.

1. Introduction

Recently, the research field of molecular spintronics has attracted much attention [1-7]. In this field, production of novel transport properties and optical properties is expected by controlling the spin degree of freedom. The spin-dependent transport properties were studied by observing the magnetoresisirance (MR) effects [1]. In researches of MR effect, the spin-function (MR effect) is the same physical phenomenon as the spin-transport, and some extrinsic effects e.g. anisotropic MR effect of ferromagnetic electrode itself easily affect the measurements. These suggest that it is hard to estimate only the spin-function of molecules. On the other hand, in researches of spin-dependent optical properties [2-7], spin-function (spin-dependent optical properties) is different physical phenomenon from the spin-transport. Therefore, the spin-function of molecules is directly estimated and extrinsic effects can be excluded. One of the hot topics in this research field is the research using organic light-emitting diode (OLED) [2-7]. Realization of circular polarization as a novel function of OLEDs is a great challenge, and will be a milestone in the molecular spintronics, as in the case of inorganic spintronics that GaAs-based LED shows circular polarization due to spin-injection [8].

The circular polarization of the OLED with a fluorescent molecule tris-(8-hydroxy-quinolinato)-aluminum (Alq$_3$) and with a ferromagnetic metal Fe cathode as a spin-injector was observed, and degree of circular polarization ($P$) was 1.0 % at 2 T [5, 6]. In the fluorescence process that is the luminescence process derived from the excited singlet state, spin-orbit interaction for the generation of circular polarization is small. Nevertheless, the circular polarization due to spin injection was observed with Alq$_3$ [5, 6]. Therefore, by using the phosphorescence that is the luminescence from the excited triplet state with large spin-orbit interaction, the circular polarization efficiently generates, and the achievement of larger $P$ is expected. In this study, the OLED with a phosphorescent molecule tris-(2-
phenylpyridine)-iridium [Ir(ppy)₃] [9] and with an Fe cathode was fabricated, and the circular polarization properties were investigated. And, it was focused that degradation processes of OLEDs depended on the operation methods [constant voltage (CV) and constant current (CC)]. One reason of OLED degradation is modification of molecules by heat due to operation current. The modified molecules don’t show luminescence, become electrical resistance in OLEDs, and finally, work as dark spots in the luminescence area of OLEDs. That is to say, the number of emissive molecules in OLEDs decreases over time. Because the thermal damage at CC operation is stronger than that at CV operation, the degradation at CC operation is faster than that at CV operation. In this study, P of OLEDs was measured by using the two operation methods, in order to study the effect on P derived from the degradation property difference of OLEDs between the two operation methods.

2. Experimental method

2.1. OLEDs fabrication
Our OLEDs consist of an ITO (In₂O₃ + SnO₂ 10 wt%) transparent anode (thickness, 150 nm), a 4,4’-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (α-NPD) hole transport layer (40 nm), a 4,4’-bis(9-carbazolyl)biphenyl (CBP) doped with Ir(ppy)₃ 10 vol% emissive layer (20 nm), a 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) electron transport layer (40 nm), an aluminum-oxide (Al-O) tunnel barrier (2 nm) to utilize the tunneling process for efficient spin-injection [10], an Fe (or Al for comparison) cathode M (20 nm) and an Al capping cathode (120 nm). Our fabrication process is as follows: On an ITO film pre-coated on a glass substrate, each molecular layer was sequentially formed by thermal evaporation under high vacuum (base pressure < 1.0 × 10⁻⁶ Pa). Next, Al for making of Al-O layer was deposited by using electron beam (EB) under high vacuum (base pressure < 1.0 × 10⁻⁷ Pa). After natural oxidization of the surface of the Al film, Fe for M, and subsequently, Al for capping cathode were deposited by EB deposition under high vacuum (base pressure < 1.0 × 10⁻⁷ Pa).

2.2. Characterization of OLEDs
In one OLED, measurements by both operation methods of CV and CC cannot simultaneously be carried out. If the measurements by the two operation methods are continuously carried out, the degraded OLED must be used at the latter characterization. Therefore, two pristine OLEDs were prepared for characterization under an equal condition.

An optical system equipped with a lock-in technique [5] was used to evaluate P of OLEDs. At CV operation, an OLED was operated by a DC bias voltage of 12 V and a rectangular modulation voltage (amplitude, 0.1 V; frequency, 220 Hz). At CC operation, an OLED was operated by a DC bias current of 0.8 mA and a rectangular modulation current (0.1 mA; 220 Hz). At P measurements, directions of the light-emitting and an external magnetic field must be parallel because the component of magnetic field perpendicular to the light direction modifies the polarization of light. In this study, bottom emission of OLED was used. Therefore, an external magnetic field was applied perpendicular to OLED substrates. The magnetic field was swept up from 0 to 1.6 T, subsequently down to -1.6 T, and again up to 0 T. The P is defined as (σ⁺ - σ⁻)/(σ⁺ + σ⁻) × 100 (%). Here, σ⁺ and σ⁻ indicate components of right and left circular polarization, respectively. Each component is detected by a photo-diode. In our system, σ⁺ and σ⁻ are measured individually and simultaneously. It seems that the magnetic field effect that the luminance of OLEDs depends on the applied magnetic field [11] is negligible.

Magnetic properties were measured with a SQUID magnetometer up to ±7 T. The magnetic field was applied perpendicular to the sample substrate, corresponding to the set up of P measurements.

3. Results and discussion

3.1. Degradation properties of OLEDs
Figure 1 shows time-decay properties of photo-current corresponding to the right circular polarization intensity of OLEDs with M = Fe at CV operation (solid circles) and at CC operation (open circles).
Each value of photo-current is normalized by the initial value. Apparently, the photo intensity at CC operation is more stable than that at CV operation, as similar to Ref. 12. However, the degradation at CC operation is faster than that at CV operation because CC operation affects device degradation more strongly than CV operation. Half-lives of OLEDs over 30 min at both operation methods were long enough to measure the $P$ of OLEDs because each measurement time for $P$ was 30 min in our optical system.

3.2. Circular polarization of OLEDs

Figures 2(a) and (b) show external magnetic field dependences of $P$ at CV operation of an OLED with $M = \text{Al}$ and of an OLED with $M = \text{Fe}$, respectively. An OLED with $M = \text{Fe}$ showed circular polarization, whereas no circular polarization was observed from an OLED with $M = \text{Al}$ [7]. Figure 2(c) shows an external magnetic field dependence of $P$ at CC operation of another OLED with $M = \text{Fe}$. Even at CC operation, an OLED with $M = \text{Fe}$ showed circular polarization. The $P$ of both OLEDs with $M = \text{Fe}$ increased linearly with increasing an external magnetic field, and the maximum $P$ (corresponding to $P$ at 1.6 T) was 0.4 % at CV operation and 0.6 % at CC operation. Figure 2(d) shows a magnetization curve of an OLED with $M = \text{Fe}$. In the range of low magnetic field, the magnetization of Fe cathode increases linearly with increasing the magnetic field, due to the shape magnetic anisotropy of Fe cathode. That is to say, the linear change in $P$ of OLEDs with $M = \text{Fe}$ can be attributed to the magnetization process of the Fe cathode. Those behaviours were in good agreement with the $P$ of OLED with Alq3 [5], and it was suggested that the circular polarization was mainly due to spin-injection.

$P$ was independent of the difference of device degradation processes derived from the difference between the two operation methods. Therefore, at $P$ measurements, CV operation is better than CC operation because the degradation at CC operation is faster than that at CV operation. However, the $P$ in this study is still small compared with the ideal value expected from the spin-polarization at Fermi energy of the Fe cathode, 45 % [13]. For production of circular polarization, not only the optical transition process in the emissive molecules, but also highly efficient spin-injection and spin-transport into emissive molecules are important. At present, spin-injection and spin-transport are inefficient in OLEDs. Improvement of $P$ by efficient spin-injection and spin-transport is one of next issues.

4. Summary

Circular polarization of OLED with an Fe cathode and with an Ir(ppy)$_3$ was observed. The maximum $P$ was 0.4 % at CV operation and 0.6 % at CC operation. $P$ was independent of device degradation process. Both the maximum $P$ values were much smaller than the value expected from the spin-polarization at Fermi energy of the Fe cathode. Efficient spin-injection and spin-transport into emissive molecules are expected for improvement of $P$. 

Figure 1. Time-decay properties of photo-current corresponding to the right circular polarization intensity of OLEDs with $M = \text{Fe}$ at constant voltage operation (solid circles) and at constant current operation (open circles). Each value of photo-current is normalized by the initial value.
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Figure 2. External magnetic field dependences of $P$ of (a) an OLED with $M = $ Al at CV operation, (b) an OLED with $M = $ Fe at CV operation, and (c) an OLED with $M = $ Fe at CC operation. (d) A magnetization curve of an OLED with $M = $ Fe.