Electroluminescence enhancement of the phosphor dispersed in a polymer matrix using the tandem structure

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An alternating current driven electroluminescence (EL) device consisting of a phosphor dispersed in a polymer matrix device was fabricated as a tandem structure. This structure can be formed by duplicating the emitting and conducting layers. The EL device with the tandem structure, particularly the device with the triple emitting layer, was six times brighter than (1460 cd/m² at an alternating voltage application of 50 V) the structure with a single emitting layer. This tandem structure plays important roles by increasing the chance of electron–hole tunneling into the phosphor with leading to an increase in brightness by combining the light emitted from several emitting layers in a device. In addition, the adoption of a spin-coating method for the deposition of an emitting layer can allow the production of a dielectric part on the lower-lying emitting phosphor powder particles. The implementation of a dielectric part and emitting part by one spin-coating procedure simplifies the overall fabrication process, particularly for the tandem structure. The significant increase in brightness with each additional emitting layer as well as a facile fabrication process would help to make the EL device a competitive candidate in future displays and lightings.

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1. Introduction
Recently, considerable research effort has been poured into future potential flat panel displays [1–5] beyond liquid crystal displays and plasma display panels, which are both commercially available. Among these candidates, alternating current (AC) thick-film powder electroluminescence (EL) devices have attracted interest owing to their low cost and a simple fabrication process with the ability for mass production [6–9]. This EL structure is composed of a top electrode, an emitting layer, a dielectric layer, and a transparent electrode. Since AC EL is light emission under a high electric field, a dielectric layer is needed to prevent catastrophic dielectric breakdown in the device. Despite the merits of EL devices, such as an easy fabrication process and scalability to a large size for EL displays, the practical applications of AC thick-film EL devices are currently limited to backlighting in cellular phones. This is mainly due to the insufficient brightness of EL devices compared to other types of flat panel displays. More research on materials and structures for these devices will help overcome the key issues in EL, such as low brightness, relatively short lifetime and high operation voltages [10–13].

In this paper, we propose a tandem structure for an AC thick-film EL device with a multiple emitting layer. This tandem structure can help overcome one of the main weak
points of the EL device, i.e., low brightness. This structure enhances the brightness of an EL device by combining the light emitted from several emitting layers (in this study up to three layers), which is similar to semiconductor multiple quantum wells or tandem solar cells [14,15]. In addition, since the capacitance of a device is increased by the parallel connection of the component emitting layers, the tandem structure would increase the chance of electron–hole tunneling in the phosphor leading to an increase in brightness. To simplify the fabrication process, a spin-coating method was also used to deposit the emitting layer. Since the dielectric part was formed on the phosphor powder particles during spin-coating, the spin-coating method can reduce the fabrication process to a single processing step instead of the two steps generally required [16].

2. Experimental

Fig. 1 shows the structure of the tandem EL device. The emitting layers are multiply stacked and the transparent conducting electrode layers are sandwiched between the adjacent emitting layers. The fabrication process for the tandem structure is as follows. An emitting layer was spin-coated on an indium doped tin oxide (ITO)-coated glass substrate at 1000 rpm for 40 s using the emitting paste composed of ZnS:Cu,Cl EL green phosphor powder (Sylvania, GG44) and an organic binder (EL-Korea, ELPR530) as a polyvinylidene fluoride (PVDF) based polymer [17]. The phosphor to binder weight ratio is 1/2. The spin-coated emitting layer was dried at 130 °C for 30 min, which yielded two separate layers by gravitation. The organic-based dielectric part was positioned on the emitting part, which was composed of phosphor particles. This spin-coating process simplified the fabrication of a tandem structure which will be explained later. An ITO transparent conducting layer was sputtered on top of the emitting layer. For a tandem structure, the coating process for the emitting and conducting layers was carried out repetitively. In this study, three different tandem structures were prepared – one, two, and three emitting layer(s). After forming the multiple emitting layer, an aluminum thin film as a top electrode was deposited on it by DC sputtering.

The light emission characteristics of the three different structured EL devices were measured under ambient conditions by varying the applied AC voltage and frequency.

Fig. 1 shows the measurement system providing the electrical power to the device. In the tandem structure, the electrical wiring was connected in parallel to each emitting layer. The middle transparent electrode was shared by the neighboring upper and lower emitting layers. A sinusoidal AC voltage generated by the combination of a conventional function generator (Agilent, 33250A) and amplifier (Trek, P0610B-K) was applied to the device. An oscilloscope (Hewlett-Packard, 400D) was used to monitor the applied voltage. All AC readings are the peak-to-peak values. The absolute brightness was measured using a luminance colorimeter (Topcom, BM-7). After measuring the light emission, the morphology of the tandem structure of the emitting layers and intervening conducting layers was examined by field emission scanning electron microscopy (FE-SEM, Hitachi S-4200).

3. Results and discussion

The spin-coating method allows the deposition of two parts (an emitting phosphor part and a dielectric part in an emitting layer) in only one spin-coating because the tandem structure inherently requires the deposition of many component layers compared to the conventional single emitting layered EL structure. After spin-coating and consecutive drying of the emitting layer, most of the remaining organic binder, which would become an organic-based dielectric part, was located on and beside the phosphor powder particles due to the low viscosity of the emitting paste. However, virtually no organic binder was located under the phosphor powder particles due to the difference in density between the powder (4.1 g/cm3) and binder (1.8 g/cm3) during the spin-coating process. As shown in Fig. 2, this separation yielded the simultaneous formation of a phosphor-based emitting layer part at the low region and an insulating dielectric layer part at the upper region. Therefore, the deposition of a dielectric layer can be omitted when this spin-coating process is used. This omission is difficult to obtain using the screen-printing method because the high-viscosity nature of the emitting paste for printing results in incomplete coverage over the phosphor particles. This incompleteness in coverage leads to the formation of pinholes in the emitting layer, which is a serious failure mechanism in EL devices [3]. This can be explained by the fact that the paste for the spin-coating method is thinner, i.e., lower viscosity, than that for the screen-printing method due to the difference in the film deposition mechanism. The screen-printing method has practical problems for the fabrication of a tandem structure because many deposition processes are necessary for the deposition of dielectric layers. Furthermore, a transparent electrode can be broken easily by the squeeze pressure during the deposition of emitting and dielectric layers in the screen-printing method. Consequently, the spin-coating is a suitable method for the tandem structure of an EL device.

In AC thick-film EL devices, the total thickness of the emitting and dielectric layers is important because it determines the intensity of the electric field for a given voltage. Since the brightness of an EL device is a function
of the applied electric field, the brightness can be strongly affected by the layer thickness [18,19]. This suggests that using small phosphor powder particles, i.e., reduced thickness of the emitting layer, would result in high brightness. For this reason, an emitting layer as thin as possible was fabricated, i.e. one monolayer of phosphor particles. Fig. 2(a) shows a cross-sectional SEM image of the single emitting layer structure, where the mean thickness of the layer was approximately 15 μm. The average thickness of the two components in the emitting layer, i.e., the phosphor particles part and dielectric part, which was formed mostly on and beside the phosphor particles, were approximately 13.5 and 1.5 μm, respectively (see Fig. 2). The same AC voltage was applied to each emitting layer of the EL device due to the parallel electrical wiring to the layers, as shown in Fig. 1, despite the serial geometric stacking of the layers. Therefore, the brightness of a tandem structure was the combination of the similar brightness of each emitting layer. The insets in Fig. 2 show emission images of a single, double and triple emitting layered structure taken by a digital camera. The emission images of Arabic numerals 1, 2 and 3 are for the single-layered, double-layered (regions marked by the solid line in Fig. 2(b) and (c)) and triple-layered structure (region marked by the dotted line in Fig. 2(c)), respectively. The brighter image comes out from the structure with an additional layer (see the insets in Fig. 2), which is explained quantitatively in Fig. 3.

Fig. 3 shows a plot of the brightness as a function of the voltage (the frequency) at a fixed frequency (voltage) at 400 Hz (50 V) for the tandem structures. Although the brightness of the single-layered structure was 100 cd/m², that of the double- and triple-layered structures was 170 and 230 cd/m², respectively, at 150 V and 400 Hz, as shown in Fig. 3(a). This does not follow the increase in brightness with increasing number of emitting layers precisely. This may be caused by the fact that the light was absorbed or scattered by other components when the light passed through the other component layers. However, when the operation of the tandem structures moved to a high frequency of 12 kHz, the brightness increased substantially to 830 cd/m² (1460) for the double- (triple-) layered structure, even at a low voltage of 50 V (see Fig. 3(b)). In contrast, the single-layered structure showed a brightness of only 230 cd/m², indicating a more than threefold increase for the tandem structure. Since the emission mechanism in ZnS:Cu,Cl phosphor is different at low and high frequencies [20–23], this might affect the different multiple increases in brightness of the tandem structure. At the low frequency, a green emission (520 nm) transition occurred from Cl on a S site (ClS) to Cu on a Zn site (CuZn) [6]. However, at high frequency, a blue transition (440 nm) occurred from ClS to interstitial Cu (Cui) [23].

All the devices in Fig. 4(a) showed a decrease in capacitance, as measured using a LCR meter at 0.1 V, with increasing frequency. The magnitude of the capacitance at the actual driving voltage of the EL device ranged from 30 to 150 V, which might be different from the measured
capacitance at 0.1 V. However, it is reasonable to assume that the tendency of the measured capacitance reflects the qualitative behavior of the actual capacitance among the devices operated at 30–150 V. The capacitance of the single, double and triple emitting layer at a frequency of 12 kHz was 1.7, 4.7 and 9.8 nF, respectively. This can be explained by considering the capacitive characteristics of the emitting layer in the EL device. The capacitance was increased by the emitting layer due to their parallel connection in the electrical wiring. Fig. 4(b) presents the brightness enhancement ratios of the double-layered (circular line) and triple-layered (square line) structures to the single-layered structure. At frequencies <1 kHz, the enhancement ratio was decreased slightly, where the range of brightness enhancement of the single-layered to double- (triple-) layered structures was 1.5–1.7 (2.1–2.6). The ratios of the brightness enhancement increased at frequencies >1 kHz (the range of double to single: 2.1–3.7 and triple to single: 3.2–6.3). The brightness enhancement of the tandem structured EL device at the high capacitance and frequency can be interpreted as follows. In the ZnS:Cu,Cl phosphor, Cu$_x$S conducting needles are formed by the Cu concentration exceeding the solubility limit in ZnS. Electrons and holes are injected into the host lattice (ZnS) at opposite ends of each Cu$_x$S needle in the ZnS–Cu$_x$S interface by the high local electric field \[24,25\]. Electrons are trapped in the shallow Cl$_x$ donor site, whereas holes are trapped by the Cu recombination centers. When the electric field is reversed, the emitted electrons recombine with the trapped holes to produce light. Therefore, the increase in capacitance of the tandem EL device led to a high probability of tunneling charge carriers at the interface between the ZnS–Cu$_x$S interface. This large charge density due to the increased capacitance based on the equation of charge, \(Q = CV\), would increase the brightness of an EL device. Furthermore, the high frequency applied to an EL device would increase the chance of electron–hole pair recombination because light emission from an EL device normally occurs at the moment of the field reversal \[3\]. As a result, the brightness of the tandem EL devices is proportional to the capacitance by the increased electron–hole tunneling and recombination at a high frequency of 12 kHz. This would lead to large increase in the brightness of the tandem EL devices. The ratio of the increment brightness of single-layered to double- (triple-) layered structure was 3.6 (6.3) at a frequency of 12 kHz. At the same frequency, the ratio of the increment capacitance of the single-layered to double- (triple-) layered structure was 2.8 (5.7).

The capacitive reactance, \(X_C\), was calculated to further examine the dependency of the brightness on the
Fig. 5. Capacitive reactance vs. frequency curve with the y-log scale for the tandem EL device.

capacitance and frequency in the tandem structure. \( X_C \) can be written as \( X_C = \frac{1}{(2\pi f C)} \Omega \), where \( f \) is the frequency of an applied voltage and \( C \) is the capacitance of an EL device. This \( X_C \) value has a strong influence on the brightness of an EL device [10]. A decrease in \( X_C \) (high capacitance and frequency) can lead to an increase in the tunneling charge carriers at the ZnS–CuS contact. Figs. 3(b) and 5 show that the brightness increased rapidly with a substantial decrease in \( X_C \). Similar results were reported in Ref. [10]. The EL device suggests that a low \( X_C \) value generally results in high brightness. The enhancement in the brightness of the double and triple emitting layer along with the simple lamination process of the spin-coating has potential for EL devices in flat panel displays.

4. Conclusion

A tandem structure for powder EL devices was fabricated by spin-coating an emitting paste composed of ZnS:Cu,Cl green phosphor powder particles and a PVDF based organic binder. Three different structures were prepared with one, two, and three emitting layer(s). The capacitance of the tandem EL device increased due to their parallel connection in the electrical wiring. This tandem structure EL device increases the probability of electron–hole tunneling into ZnS lattice and recombination electron–hole, and combines the light emission from each emitting layer. An approximately six fold increase in brightness for triple emitting layer was obtained at the high frequency regime. In addition, the tandem EL device was fabricated using a fast and simple process because the emitting phosphor part and dielectric part in the emitting layer were deposited by a single spin-coating process. This tandem structure can be a potential candidate for flat panel EL displays.

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References

[17] The brand name of product is ELPR530, and the detail information on this product can be found from the company webpage (http://www.el-korea.co.kr).