Effect of field enhancement on inorganic powder electroluminescence using short carbon nanotubes

Jin-Young Kim a, Min Jong Bae b,c, Shang Hyeun Park b,*, Taewon Jeong b, Sunjin Song b, Jeonghee Lee b, Intaek Han b, Ji Beom Yoo c, Donggeun Jung a, SeGi Yu d,*

a Department of Physics, BK 21 Physics Research Division, Sungkyunkwan University, Suwon 440-746, Republic of Korea
b Electronics Material Lab., SAIT Samsung Electronics, Yongin 446-712, Republic of Korea
c SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon 440-746, Republic of Korea
d Department of Physics, Hankuk University of Foreign Studies, Yongin 449-791, Republic of Korea

ARTICLE INFO
Article history:
Received 4 June 2010
Accepted 11 August 2011
Available online 7 September 2011

ABSTRACT
Inorganic powder electroluminescence (IPEL) devices with the insertion of a carbon nanotube (CNT) layer were investigated to verify the effect of the increased local field produced by CNTs on electroluminescence (EL). To increase the field strength effectively, the CNTs were shortened using the cryogenic crushing method. IPEL devices with the insertion of a short CNT layer exhibited an increase in brightness and efficiency with increasing amount of CNTs. The local field enhancement by CNTs, further enlarged by the triple-junction, could increase the field strength applied to the phosphor, resulting in improved EL performance. In addition, short CNTs in an EL device can lead to field enhancement without an unintentional current flowing into the device.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction
Carbon nanotubes (CNTs) are considered to be attractive field emitters, because of their high electrical conductivity and high aspect ratio with nanometer sizes [1-3]. Studies on their applications as electronic devices have produced field emission displays [4] and backlight units for liquid crystal displays [5]. Recently, another type of field enhancement effect of CNTs was reported in the field of inorganic powder electroluminescence (IPEL), where a mixture of CNTs and cathodoluminescent (CL) phosphor can produce electroluminescence (EL). To increase the field strength effectively, the CNTs were shortened using the cryogenic crushing method. IPEL devices with the insertion of a short CNT layer exhibited an increase in brightness and efficiency with increasing amount of CNTs. The local field enhancement by CNTs, further enlarged by the triple-junction, could increase the field strength applied to the phosphor, resulting in improved EL performance. In addition, short CNTs in an EL device can lead to field enhancement without an unintentional current flowing into the device.

In general, EL is a phenomenon of light emission of a material under the influence of an electric field. The first inorganic EL was observed from oil suspended ZnS powder under an alternating current (AC) voltage by Destriau [7]. An EL device is usually a sandwiched structure of a light-emitting layer between two electrodes. Among the many EL device structures, AC-type thick-film IPEL structures have attracted considerable attention as a potential candidate for illumination and display applications, due primarily to the advantages in the substrate flexibility and process, such as the simple fabrication of large-sized panel, low cost manufacturing and no requirement of vacuum processing [8-11]. In general, the structure of an IPEL device is composed of an electrode/dielectric/phosphor/electrode/substrate [12,13], and each component was fabricated using the screen-printing method [14]. Despite the simple fabrication processes in IPEL devices, the actual application of IPEL devices have been confined to backlight units in cellular phones due mainly to their insufficient performance, such as...
low brightness and efficiency [15,16]. Considerable effort has been made to improve the properties of IPEL devices—using organic dye-phosphor composites [17] and adoption of a multi-emitting-layer structure [18]. However, high brightness with a simple structure operated at relatively low voltage and low frequency is still required for EL devices as one of future flat panel displays.

This paper reports the results of the local electric field effect, which might be enlarged by the existence of the triple-junction [19,20], in IPEL devices by inserting a separate layer of CNTs between the dielectric and phosphor layers. To prevent an unintentional current by the CNT networks, the length of the CNTs was shortened using a cryogenic crushing method [21]. This study clarifies the brightness improvement by the local electric field from the CNTs, and proposes a new structure to construct highly efficient IPEL devices.

2. Experimental

2.1. Preparation of component layers

The top-emission type structure was used for the IPEL devices (Fig. 1(a)) [22]. Fig. 1(b) shows a cross-section scanning electron microscopy (SEM) image. The materials of the component layers were prepared as follows. Single-wall carbon nanotubes (SWCNTs, Hanwha Nanotec, ASP-100F) were shortened using the cryogenic crushing method for 20 or 30 min [21]. An ethanolic solution of shortened SWCNTs was dispersed further in dichlorobenzene and treated by ultra-sonication for 2 h. The dielectric paste was prepared by mixing the BaTiO3 powder (Samsung Fine Chemicals, SBT03) and a fluoro-resin-based organic binder (ELK Corp., ELPR530) using ethylene glycol mono-butyl ether acetate as the solvent. The light-emitting paste was prepared using the same method of a dielectric paste, except that ZnS:Cu,Cl phosphor (Sylvania, GG44, encapsulated by alumina) was used instead of BaTiO3.

2.2. Formation of EL devices

Device fabrication was performed using step-by-step coatings of the layers. First, a dielectric layer was deposited on an aluminum-coated glass substrate by screen-printing and dried at 130 °C for 30 min. A shortened SWCNT suspension was then deposited on the dielectric layer by spin-coating at various coating speeds (300, 400, and 500 rpm) and dried at 100 °C for 30 min. The phosphor layer was then deposited on the SWCNT layer by screen-printing and dried at 130 °C for 30 min. Finally, indium tin oxide (ITO) as a top electrode was deposited on the emitting layer by dc sputtering using an ITO target (DASOM RMS, xIn2O3–ySnO2).

2.3. Characteristic of EL devices

The characteristics of the devices were measured by applying a sinusoidal AC voltage under an atmospheric environment. All the AC readings in this paper refer to the peak-to-peak values. Combined equipments composed of a conventional function generator (Agilent, 33250A) and a power amplifier (Trek, P0610B-K) were used to generate the AC voltages. An oscilloscope (Hewlett-Packard 400D) was connected to an IPEL device to monitor the actual value of the applied high voltage. The brightness of the IPEL devices was measured using a luminance colorimeter (Topcon, BM-7). The field emission characteristics of the shortened SWCNTs were measured in a vacuum chamber with a diode type configuration under 1×10⁻⁷ torr, where the CNTs were deposited on the ITO-coated glass substrate as a cathode plate and the distance between the cathode and anode (a bare ITO substrate) was maintained using 400 μm-thick glass spacers.

3. Results and discussion

The untreated SWCNTs (roughly 3 μm long) were shortened to less than the sub-micrometer range after a cryo-crushing time of 20 min [21]. The Raman spectral peak at 1325 cm⁻¹ represents the disorder state of carbon atoms in the graphitic structure, known as the D-band. According to Fig. 2, the D-band intensities of the SWCNTs increased with increasing crushing...
time, where the lowest intensity was observed for the non-treated SWCNTs. The higher D-band intensity of the shortened SWCNTs originated from a relatively large amount of amorphous carbon through the cryo-crushing process [23]. In all IPEL devices in this study, the crushing time was fixed to 20 min because short SWCNTs for a crushing time of 20 min could induce effective field enhancement among various crushing times. The amount of deposited SWCNTs was controlled by the spin coating speed.

The measured luminance of each IPEL device with a layer of SWCNTs coated at 300, 400, 500 rpm was 192, 182, and 174, respectively, whereas the luminance for the no CNT was 160 cd/m² (Fig. 3). This indicates that the luminescence of IPEL was improved by the presence of SWCNTs, and the high concentration of CNT, i.e., obtained using a slow coating speed, resulted in high EL performance. The 300 rpm sample was 20% brighter than the sample without the SWCNTs [24]. The 20% improvement in the brightness is still not sufficient to solve the long-lasting brightness problem for IPEL devices, however, the adoption of a nanomaterial might hint a new direction for this problem, whereas the previous researches on EL rather focused on other issues, i.e., the crystallinity of the phosphor particle [16,25], the encapsulation of phosphor particle [26], doubling the emitting layer [9], and incorporation of organic dye [17]. Considering the recent intensive research activities in various fields to utilizing nanotechnology [27,28], this approach, i.e., using a carbon based nanomaterials, at least, might not lead to a wrong direction.

In general, an electric field in an AC IPEL device is the key governing factor for the luminance because the intensity of the luminance can be determined mainly by the intensity of an electric field [14,29]. ZnS:Cu,Cl phosphor particles have ZnS–Cu$_x$S heterojunctions, where ZnS (Cu$_x$S) is a n-type (p-type) semiconductor. When an electric field of 10$^6$–10$^7$ V/m is applied to the phosphor, the electric field induces tunneling of electrons and holes into ZnS lattice at opposite ends of each Cu$_x$S, then electrons are trapped in the Cl donor site, while holes are trapped by Cu recombination centers. At the reversal field, the emitted electrons recombine with the trapped hole to produce light [14,29]. In the present study, the SWCNT layer on the dielectric layer, and at the same time beneath the phosphor particle layer, could supply a high local electric field to the phosphor particles, which might be explained by a triple-junction type enhancement between the SWCNT, the dielectric material, and the phosphor [19]. This field enhancement could not be simply explained by considering the high geometrical aspect ratio of SWCNTs as explained in Refs. [19,20].

The existence of the triple-junction between the SWCNT, the dielectric material, and phosphor particles could be one of main reasons for this improvement. The abrupt potential change around SWCNTs, assisted by the work function difference of the surrounding dielectric and phosphor materials, could provide a considerable high electric field [20]. The recombination of holes trapped in the Cu recombination centers together with the increased electrons at the enhanced field at the reverse voltage will produce more light [14]. Therefore, the improved EL performance from the IPEL devices with a layer of SWCNTs might be explained by the enlarged electric field at the triple-junction.

To clarify the direct relationship of the IPEL performance to the field enhancement effect asserted from SWCNTs, the field emission characteristics of the shortened SWCNTs were measured for three coating speeds. Since the field emission of SWCNTs on a dielectric layer is difficult due to the insulating nature of the dielectric layer, the measurements were performed directly on an ITO-coated glass substrate. Although the magnitude of field enhancement of the shortened SWCNTs on the dielectric layer might be different from that on the ITO substrate, the tendency of the enhancing effect to field enhancement could be matched between CNTs on the dielectric layer and ITO layer. Therefore, the field emission of SWCNTs on the ITO substrate for the three coating speeds was measured and the corresponding Fowler–Nordheim (F–N) plots [30], are shown in Fig. 4. The turn-on electric fields (defined as the electric field at a current density of 10 $\mu$A/cm$^2$) were 1.6, 1.8, and 2.1 V/μm, for coating speeds of 300, 400, and 500 rpm, respectively. The dimensionless field enhancement factors ($\beta$) concerning the geometrical contribution of CNT were 4750, 4500, and 3000, respectively, and the area factors ($\alpha$), related to the number of emitting sites were 3.2 × 10$^{-8}$,

![Fig. 3 – Luminance and efficiency as a function of the driving voltage for the IPEL devices with no SWCNTs and with a layer of shortened SWCNTs prepared for three coating speeds (300, 400, and 500 rpm).](image3)

![Fig. 4 – Field emission current density as a function of the applied field for the shortened SWCNTs deposited at various coating speeds on an ITO substrate. The inset shows the corresponding Fowler-Nordheim plots.](image4)
2.6 × 10⁻⁸ cm² and 7.9 × 10⁻⁹ cm², respectively for a 300, 400, and 500 spin speed. Here, the work function of SWCNTs was assumed to be 5 eV [31]. Among these three samples, the one prepared at 300 rpm exhibited the highest field emission characteristics, which is due to the relatively high density of SWCNTs compared to the other speeds. Table 1 summarizes the geometry factor (\(b\)) and area factor (\(a\)) of the shortened SWCNTs on the ITO substrate, and the luminance of the IPEL devices with a layer of shortened SWCNTs.

<table>
<thead>
<tr>
<th></th>
<th>300 rpm</th>
<th>400 rpm</th>
<th>500 rpm</th>
<th>No CNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) (10⁻⁸ cm²)</td>
<td>3.2</td>
<td>2.6</td>
<td>0.79</td>
<td>–</td>
</tr>
<tr>
<td>(b)</td>
<td>4750</td>
<td>4500</td>
<td>3000</td>
<td>–</td>
</tr>
<tr>
<td>Luminance (cd/m²)</td>
<td>192</td>
<td>182</td>
<td>174</td>
<td>160</td>
</tr>
<tr>
<td>Luminance increment</td>
<td>20%↑</td>
<td>14%↑</td>
<td>8.4%↑</td>
<td>–</td>
</tr>
</tbody>
</table>

In general, the local electric field is increased in proportion to the field enhancement factor, \(\beta\), based on the equation, \(E = \beta \sqrt{V}\). A layer of SWCNTs with a high \(\beta\) value would enhance the electric field with a help of the triple-junction, facilitating electron tunneling and acceleration in the phosphor layer. In addition, the higher \(a\) value, representing a larger number of enhancing sites in field emission, would provide more recombination sites in EL, producing brighter luminescence.

To investigate the length effect of the SWCNTs, three different IPEL devices, i.e., with no SWCNTs, with shortened SWCNTs, and with untreated long SWCNTs, were prepared at a fixed spin coating speed of 300 rpm. Their luminescence characteristics were measured at driving voltages up to 150 V and 400 Hz. According to Fig. 5, the luminance of the device with a layer of SWCNTs, whether shortened or untreated, was higher than that with no SWCNTs.

On the other hand, the EL efficiency of the device with the untreated SWCNTs was similar to that without SWCNTs, and lower than the one with the shortened SWCNTs. The efficiency, \(\eta\), was obtained from the equation, \(\eta = \pi \times \frac{P}{L} (\text{lm/W})\) [14], where \(L\) is the luminance. The lower efficiency of the untreated SWCNT device was caused by the relatively high current flow during the EL operation. This might be caused by the interconnection of long SWCNTs producing a waste current with no contribution to EL [32]. On the other hand, the device with the shortened SWCNTs showed similar current flow with respect to the one without SWCNTs, indicating much fewer conducting paths in the shortened SWCNT layer. Therefore, the IPEL device with shortened SWCNTs exhibits higher efficiency and high luminescence.

### 4. Conclusions

A series of IPEL devices was fabricated with insertion of a shortened SWCNT layer between the phosphor and dielectric layers. The shortened SWCNTs were prepared using the cryogenic crushing method to effectively enhance the electric field but prevent possible conducting paths in the SWCNT layer. The EL performance improved with increasing amount of SWCNTs, reflecting the local field enhancement effect by the shortened CNTs. The evaluation of the EL efficiency for the IPEL device with long or short SWCNTs highlighted the importance of the shortened character of the SWCNTs, which increase the EL efficiency through the high luminance with low current flow.

### Acknowledgements

This work was supported in part by the National Research Foundation of Korea (NRF 2010-0011894). D. Jung was supported by grants NRF-2010-0029699 (Priority Research Centers Program). J.-Y. Kim is a recipient of the Seoul Science Fellowships of the Seoul Metropolitan Government.

### REFERENCES


[23] To compare SWCNT layer incorporated IPEL devices with other group’s devices gives much clear interpretation on the importance of a SWCNT layer. However, the fact that IPEL devices reported elsewhere [9,16,17,25,26] have different structures, materials, and operation conditions, yields to difficult in direct comparison with other devices unlike photovoltaic solar cells. Instead, the reference device, i.e., the IPEL device without SWCNTs, was fabricated and compared with SWCNT IPEL devices, which could explain the meanings of SWCNT’s contribution to EL.


