Efficiency Enhancement of Flexible Inorganic Powder Electroluminescent Devices Using the $BaTiO_3$-MWNT Composite Dielectric Layer

Fang-Hsing Wang, *Member, IEEE*, and Kuo-Feng Chen

***Abstract*—Alternating current inorganic powder electroluminescent (IPEL) devices possess many advantages including wide viewing angle, wide operating temperature range, and easily manufactured by using a screen printing process. This study developed an IPEL devices with low power consumption and high brightness on a transparent polyethylene terephthalate substrate by introducing a composite dielectric layer, which was formed by incorporating single- or multiwall carbon nanotubes (SWNTs or MWNTs) into the $BaTiO_3$-based dielectric layer. The luminous efficiency of the developed devices, called the IPEL: carbon nanotubes (CNT) devices, increased with appropriate incorporation ratios of CNTs, regardless of SWNTs or MWNTs. The optimal device performance was achieved with a 0.5 wt% mixing ratio of MWNTs, in which the power consumption of the device decreased 33.7% and the luminous efficiency increased 50.9% at the brightness of 100 cd/m^2. The result of bending test with a curvature radius of 1 cm for 10^4 times showed that the IPEL:MWNT device had a superior luminous reliability and its variation of the efficiency was less than 6%. The developed IPEL:MWNT device has potential as a candidate in future flexible displays.**

***Index Terms*—Carbon nanotube (CNT), efficiency, flexible display, powder electroluminescence.**

I. Introduction

INORGANIC electroluminescence (IEL) devices possess many advantages such as low cost, high brightness, low environmental usage restriction etc., and are well suited for serving as flat panel displays. The primary principle of an IEL component is to utilize high electric field to inject electrons into the component so that electrons collide with luminescent centers of luminescent powders and then emit light. IEL devices are classified into two types: thin-film EL [1]–[3] and inorganic powder EL (IPEL) [3]–[6]. The former requires vacuum and high temperature process, and thus it has the shortcoming of high manufacturing cost; while the latter (IPEL) uses a low cost screen printing process, which does not require vacuum facilities. Furthermore, IPEL uses a low temperature process and thus is quite suitable for manufacturing of large-size and flexible displays. The traditional IPEL device works in extra high electric field condition and has a serious shortcoming of low luminous efficiency due to low electron injection effect [7]. A few efforts have been reported to improve the luminous efficiency of IPEL devices [8]–[16]. Especially it has been reported that carbon nanotubes (CNTs) tend to enhance electric field and thus may improve the luminous properties of IEL devices [8], [15]. Kim *et al.* [15] reported that IEL devices with the insertion of short single-wall CNTs into devices exhibited an increase in brightness and efficiency.

This work introduces either single- or multiwall carbon nanotubes (SWNTs or MWNTs) into the dielectric film of IPEL devices and creates new IPEL device structure to improve luminous efficiency. The brightness and efficiency of the proposed CNTs-incorporated IPEL (denoted IPEL:MWNT or IPEL:SWNT hereafter) device as a function of current density were investigated. The mechanism of improved efficiency for the developed device was proposed. Bending test with a curvature radius of 1 cm was also studied for flexible display applications.

II. Experimental

Fig. 1 shows the schematic structure of the proposed IPEL:CNT devices. A transparent conducting ITO film, as a top electrode, with a thickness of 200 nm was sputtered on a transparent polyethylene terephthalate (PET) substrate with an area of 4.5 cm $\times$ 4.5 cm. A ZnS-based phosphor paste (LuxPrint 8150L, DuPont Inc.) with a particle size of about 20 μm was subsequently laminated on the ITO film by screen printing and then baked at a temperature of 130 °C for 10 min [Fig. 1(b)]. The thickness of the dry phosphor layer was measured by a surface microprofile machine (Kosaka Laboratory Ltd, ET4000LK) and was about 40 $\pm$ 2 μm. Afterward, the first $BaTiO_3$-based dielectric layer (LuxPrint 8153, DuPont Inc.) with a particle size of about 0.1 μm was coated on the phosphor layer using screen printing and then baked at 130 °C for 5 min [Fig. 1(c)]. The dry film thickness and dielectric constant of the first dielectric layer were 7 $\pm$ 2 μm and 35, respectively. The second dielectric layer is a composite layer which is composed of the first dielectric material and CNTs, which are either MWNTs (Xintek Inc, field emission grade, Thermal CVD method) or SWNTs (Carbon-Lex Inc, AP-grade, Arc discharge method). The MWNT was with a diameter of 8 nm, a length of 20 μm, and an electric field enhancement factor (β = length / diameter) of 2500. The

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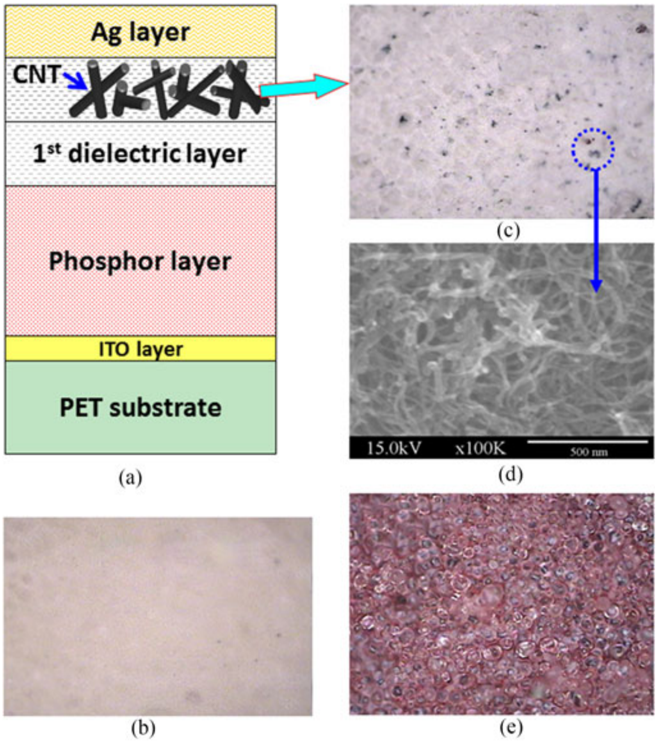

Fig. 1. (a) Schematic structure of the IPEL:CNT device and micrographs of the (b) phosphor, (c) and (d) dielectric, and (e) MWNT.

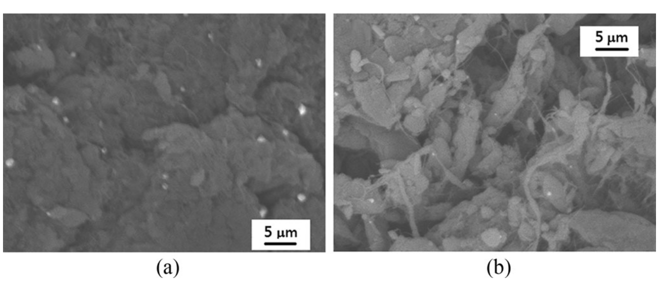

Fig. 2. SEM micrograph of the MWNT powders before (a) and after (b) pre-treatment process.

SWNT was with a diameter of 1 nm, a length of 2 μm, and an electric field enhancement factor of 2000. The contents of CNTs in the composite paste were 0.5, 1.0, and 2.0 wt%. The MWNT powders need to pre-treat because too large particle size may increase difficulty during mixing and distribution process. In the pre-treatment process, MWNT powders were grinded by disperse device (1KA–T18 basic) to reduce particle size. Fig. 2 exhibits SEM micrographs of the MWNT powders before and after pre-treatment process. Their particle size reduced from 10–50 μm to 1–5 μm after the pre-treatment process. Afterward the MWNT powders were filtered, dried, and mixed with the dielectric paste. The mixed composite CNT-dielectric paste initially dispersed using a three-roller equipment and subsequently de-bubbled using a planetary centrifugal mixer. Then the composite dielectric paste was screen printed on the first dielectric layer and then baked at 130 °C for 5 min [Fig. 1(d)]. The dry film thickness of the second dielectric layer was about

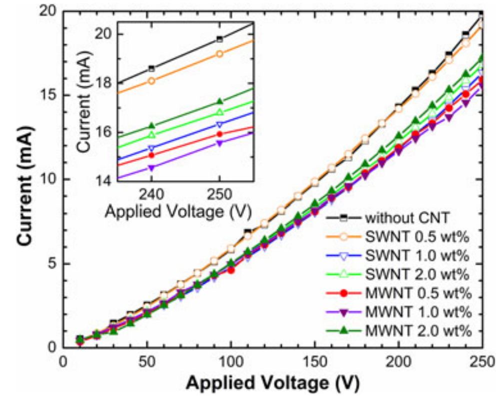

Fig. 3. Current-voltage characteristics of all IPEL (without/with CNTs) devices.

7 ± 2 μm. Fig. 1(e) shows the micrograph of the MWNT-dielectric composite layer. It can be seen that MWNTs are well dispersed in the dielectric layer. Finally, the rear electrode (Ag, LuxPrint 9145, DuPont Inc.) was coated on the composite dielectric layer using screen printing and then baked at 130 °C for 5 min. The dry film thickness of the Ag electrode was approximate 12 ± 2 μm with a sheet resistance of below 50 m$\Omega/\square$. A cleaning process was performed before electrical measurement using a dust-free cloth and industrial alcohol.

The IPEL devices are measured by a hybrid electrical-optical measurement system, which consists of a function generator (Tektronix, AFG-3021), a piezo driver/amplifier (TREK, PZD-350), and a colorimeter (KLEIN, K8). For EL measurement, biased sinusoidal pulses were applied between the two electrodes at a frequency of 1 kHz. The applied ac voltage and consumed current were monitored by an oscilloscope (Tektronix, TDS-1012). Brightness of the IPEL devices was measured with the colorimeter from the PET side. It is noted that luminous measurement is performed in a dark room to reduce noise caused by environment light.

III. Results and Discussion

Fig. 3 shows the root-mean-square (RMS) current-voltage relationship for all IPEL devices. It is clearly observed that the current gradually increases when the applied voltage is increased from 0 to 250 V. Under a fixed voltage of 240 V, the consumed current for the proposed samples in ascending order are 1.0 wt%-MWNT, 0.5 wt%-MWNT, 1.0 wt%-SWNT, 2.0 wt%-SWNT, 2.0 wt%-MWNT, 0.5 wt%-SWNT, without CNT, as shown in the inset of Fig. 3.

Fig. 4 shows the brightness and luminous efficiency of the IPEL devices as a function of current density (RMS values) with various CNT mixing ratios. The brightness of all the samples increased as the current density increased regardless of CNT types and contents. Under the condition of a brightness of 100 cd/m^2 and an operating frequency of 1 kHz, the current densities were 0.240, 0.252, and 0.284 mA/cm^2 for the 0.5, 1.0 and 2.0 wt%-MWNT samples as well as 0.334, 0.271, and 0.275 mA/cm^2 for the 0.5, 1.0 and 2.0 wt%-SWNT samples, respectively. This result indicates that CNT-incorporated

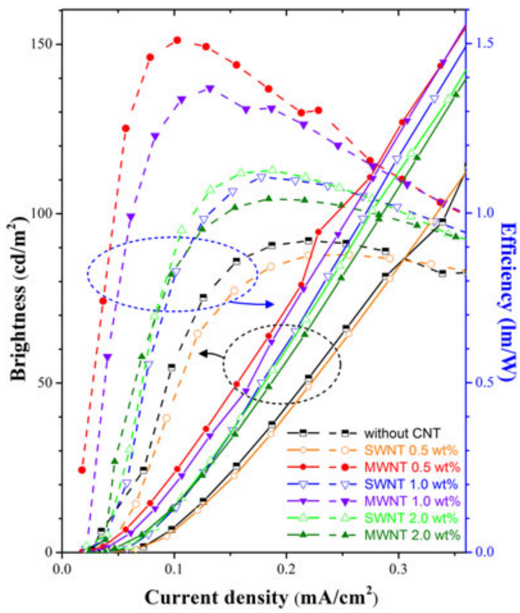

Fig. 4. Brightness and efficiency of the IPEL devices as a function of current density with various CNT ratios.

TABLE I
POWER DENSITIES OF VARIOUS IPEL DEVICES AT THE BRIGHTNESS OF 100 cd/m^2

Sample Type	w/o CNT	SWNT (wt%)			MWNT (wt%)		
		0.5	1.0	2.0	0.5	1.0	2.0
Power density (mW/cm^2)	38.2	37.2	30.0	30.1	25.3	26.8	31.7
Power reduction ratio (%)	–	2.62	21.5	21.2	33.7	30.1	17.1

IPEL devices have lower current consumption than the traditional IPEL device (0.34 mA/cm^2) except the 0.5 wt%-SWNT sample. In addition, among various IPEL:CNT devices, the MWNT-incorporated devices consumed less average current than SWNT-incorporated ones. The sample with the mixing ratio of 0.5 wt%-MWNT achieved the maximum reduction ratio of approximate 30% in current consumption in comparison with that without CNTs. Power consumption of the devices was also calculated through applied voltage multiplying by current. Table I lists power density and power reduction ratio for various IPEL devices at the brightness of 100 cd/m^2. The power reduction ratio was calculated as compared with that without CNTs. We found that the devices with 0.5–1.0 wt%-MWNT achieved lower power consumption and their power reduction ratios were over 30%. According to Park *et al.*'s report [17], the power consumption is linearly dependent on the device capacitance. In this work, the dielectric layers have almost the same thickness for all devices except a small amount ($\leq$2 wt%) of MWNT incorporation in the second dielectric layer. It is believed that the capacitance will not significantly vary by adding such little MWNTs. Therefore, the significantly reduced power consumption and enhanced brightness of the proposed IPEL:MWNT devices should be not mainly attributed to the device capacitance.

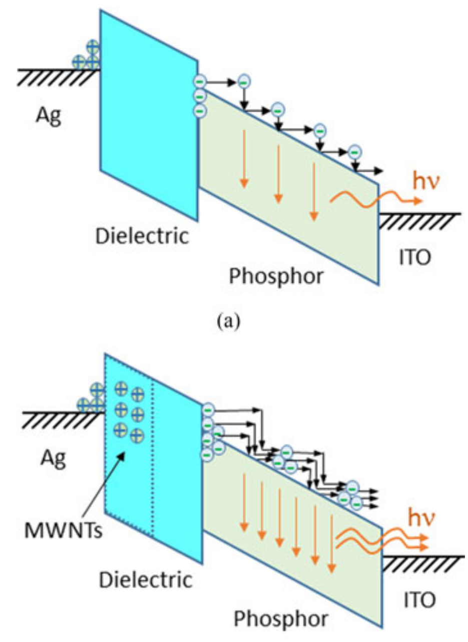

Fig. 5. Energy band diagram of (a) the traditional IPEL device and (b) the IPEL:CNT device with an electric field.

Luminous efficiency is another important characteristic for EL devices and can be estimated by the following equation:

$$\text{luminous efficiency} = \frac{\text{brightness}}{\text{power density}} \times \pi. \tag{1}$$

Refer to the Fig. 4, the luminous efficiency markedly increased after incorporating MWNTs into the composite dielectric layer because of the enhanced brightness and the reduced power consumption. Moreover, the devices incorporated with MWNTs have better luminous efficiency than those incorporated with SWNTs. As compared with the device without CNTs, the luminous efficiencies of the 0.5 wt%-MWNT sample increased by 50.9% at a constant brightness of 100 cd/m^2, and its maximum value was 1.51 lm/W, which corresponded to an increment of 64.4%. By contrast, the SWNT-incorporated devices only obtained a relatively small improvement (2.85%–27.4%) in luminous efficiency under the mixing ratios of 0.5 wt%–2 wt%.

Fig. 5 shows the band diagrams of the traditional and the IPEL:MWNT devices. When an electric field is applied between the bottom and top electrodes of the device, the electric filed in the phosphor layer is large enough to emit electrons into the conduction band. These injected electrons gain energy from the field and transport across the phosphor layer to result in impact excitation. Majority carriers in the phosphor layer are electrons [18]. The transported electrons produce luminance when they reduce from the excited state to the ground state. The appropriate CNTs existing in the dielectric layer may enhance the electric field through the following equation:

$$\Delta E_{\text{field}} = \beta \times E_C \tag{2}$$

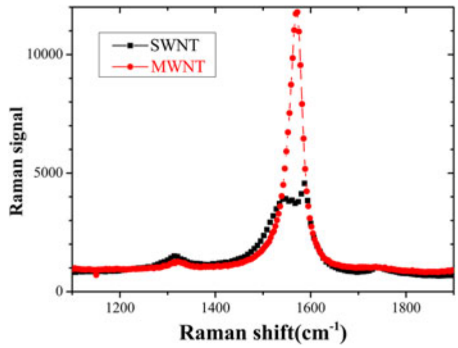

Fig. 6. Raman spectra of the SWNT and MWNT powders.

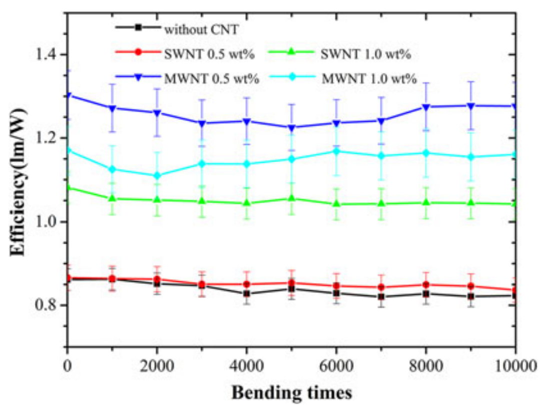

Fig. 7. Efficiency variation of the IPEL devices after the bending test with the curvature radius of 1 cm for 10 000 times. At least three meaningful data were obtained to determine the mean value and its error.

where ΔE_{field} is an increment in electric field, E_C is a CNT-enhanced electric field, and β is field enhancement factor. The increased electric field boosts the electron energy in the phosphor layer and thus more impact excitation of electrons occurs with luminescence centers, thus producing higher luminance and lower power consumption for the IPEL:MWNT devices.

Fig. 6 shows the Raman spectra of the SWNT and MWNT powders. The peak at 1350 cm^{-1} is D peak, which originates from a resonant coupling of the excitation laser with electronic states associated with disordered graphite materials; while the peak at 1580 cm^{-1} indicates a G-peak signal, which arises from the active mode E_{2g}^2, indicating the presence of crystalline graphite carbon in CNTs [19], [20]. The I_D/I_G value of the SWNTs and MWNTs were 0.295 and 0.202. The observation from Raman spectra exhibited that the degree of graphitization of the MWNTs was higher than that of SWNTs [21], [22]. Higher graphitizing can induce more sp^2 bonding, which is able to enhance electric field effect. The delocalized electrons in the orbital of sp^2 bonding have higher mobility than the localized electrons in bonds, and these delocalized electrons are easy to emit from CNTs with a built-up electric field. This result explains why the IPEL devices incorporated with MWNTs achieve better luminous performance than those incorporated with SWNTs.

Bending test is a general approach to evaluate the reliability for flexible electronic applications. Fig. 7 shows the variation in efficiency of the IPEL devices after a bending test. The test is carried out with the curvature radius of 1.0 cm for 10,000 times. The efficiency was obtained under an applied voltage of AC 100 V. The variations of efficiencies for all the IPEL:CNT devices were within 6% for the duration of the bending test. The result shows that the IPEL:CNT devices possess superior flexibility and its luminous characteristic does not considerably change after adding CNTs into the dielectric layer because of the outstanding mechanical characteristic of CNTs [23]. The abovementioned results demonstrate that the MWNTs incorporating into the dielectric layer of the IPEL devices can effectively improve the luminous efficiency and decrease the power consumption. However, excess CNTs (≧2 wt%) will deteriorate the luminous efficiency because of difficulty in CNTs dispersion in the dielectric layer. This may result in possible short-circuit in the dielectric layer and a large leakage current.

IV. Conclusion

The alternating-current IPEL devices with enhanced brightness have been developed by introducing the CNTs-incorporated composite dielectric layer into the device structure. The appropriate CNTs incorporating in the dielectric layer may decrease the current consumption and increase the luminous efficiency. The power consumption of the IPEL device with 0.5 wt%-MWNT decreased by 33.7% at a brightness of 100 cd/m^2 and its maximum efficiency increased by 64.4% as compared with that without CNTs. Results of the bending test indicated the variations of efficiencies for all the IPEL:CNT devices less than 6% and demonstrated that the developed IPEL:MWNT devices had superior flexibility and luminous reliability. The proposed IPEL:MWNT device has potential for flexible display applications.

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