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The effect of atmospheric pressure plasma treatment on the field emission characteristics of screen printed carbon nanotubes

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Abstract

The effects of pin-to-plate type atmospheric pressure plasma treatment on the field emission properties of screen printed carbon nanotubes(CNTs) were investigated using He(10 slm)/N_2(0.1 slm). The plasma treatment for 10 s decreased the turn-on field from 3.13 V/μm to 1.21 V/μm, increased the emission current, and increased the number of emission sites. When, the 10 s plasma treatment was also applied to the CNTs which were previously treated by a tape activation method, the number of emission sites were further increased, therefore, the emission uniformity was improved even though, the plasma treatment on the tape-activated CNTs increased the turn-on field slightly 0.76 V/μm to 1.25 V/μm due to the removal of long CNTs.

1. Introduction

Carbon nanotubes(CNTs) have been actively investigated as the application to field emitter of field emission display(FED) device due to their superior physical and electrical properties [1–4]. The carbon nanotube field emitters have large aspect ratios with a few ∼ tens of nm in diameter and a few micrometer in length, therefore, the field enhancement factor (β) of the carbon nanotube field emitter is known to be more than 100 times higher than that of spindt-type field emitter. Therefore, by using carbon nanotube field emitter, field emission voltage of the FED device can be lowered in addition to the stability of emission current due to its strong physical property.

CNT field emitters are generally formed on the FED device by direct growth methods using chemical vapor deposition [5,6] or by screen printing methods [7–11]. Currently, the screen printing methods are closer to commercialization because the growth of CNTs in the gate hole by the direct growth methods shows problems in the fabrication of CNT emitters such as high growth temperature, complicate process, etc. However, the screen printing methods also need to be improved for commercialization due to the poor electron emission characteristics by the irregular dispersion and misalignment of CNT field emitters and organic residue remaining on the CNTs. To remove the problem related to the screen printing methods, various CNT surface treatment methods such as adhesive taping [12], ion irradiation [13], soft rubber rolling [14], plasma exposure [15–19], etc. have been investigated. Among these methods, adhesive taping and soft rubber rolling are easy methods in removing the paste layer on the CNTs, however, these methods tend to leave residue and to destroy CNT patterns, therefore, nonuniform emission sites can be resulted. In the case of ion irradiation and plasma exposure, due to the use of vacuum processing, the processing cost is increased in addition to the difficulty in large area processing.

In this study, as a possible solution to the above mentioned problems related to screen printing, an atmospheric pressure plasma treatment by a pin-to-plate type atmospheric pressure plasma source has been used and its effects on the CNT field emission characteristics were investigated [20–22]. It is believed that, if the CNT surface treatment

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can be successfully accomplished by the atmospheric pressure plasma, the surface treatment of CNT field emitters is possible at a low cost of ownership, for a large area substrate, and by in-line.

2. Experimental

In this study, multi-walled CNTs grown by thermal chemical vapor deposition and the multi-walled CNT paste was screen printed with the size of $2 \times 2\ cm^2$ on the sodalime glass substrate coated with indium tin oxide (ITO). The screen printed CNT paste was baked at 120 °C for 10 min in the air and fired at 380 °C in a conventional oven in an N_2 environment to burn out the organic binder of the CNT paste before the atmospheric pressure plasma treatment.

Fig. 1 shows the schematic diagram of the pin-to-plate type atmospheric pressure plasma source used to treat the surface of the screen printed CNTs. The source was a modified dielectric barrier discharge having a multiple pin-type top electrode. The size of the electrodes was 100 mm width × 1000 mm length and the electrodes were made of aluminum. The multiple pin-type electrode used to ionize the gas more efficiently by generating corona discharge. Alternating current power supply (3–20 kV, 20–30 kHz) was connected to the multiple pin-type electrode and the other blank electrode was grounded. 1.5 mm thick quartz plates were located on the both of the electrodes to suppress arcing and the distance between the electrodes (air gap) was maintained at 4 mm. Between the electrodes, a gas mixture of He(10 slm)/N_2(0.1 slm) was fed to generate the atmospheric pressure plasma for the treatment of the CNT surface. The plasma treatment time was varied from 10 s to 30 s.

The CNT morphology before/after the plasma treatment was observed by transmission electron microscopy (TEM; JEOL JEM-3011) and field-emission scanning electron microscopy (FE-SEM, Hitachi S-4700). The field emission properties of CNT field emitters before/after plasma treatment were measured in a vacuum chamber with a parallel diode-type configuration at 5×10^{-6} Torr using direct current (DC) power supply. To observe the emission uniformity, phosphor/ITO/glass was used as the anode and the emission uniformity was observed by an optical microscope. The distance between the CNT field emitter and the anode was maintained at 400 μm.

3. Results and discussion

Fig. 2 shows SEM micrographs of CNT paste (a) before and (b) after the plasma treatment. The atmospheric pressure plasma was generated using He (10 slm)/N_2(0.1 slm) at the input voltage of 10 kV. The plasma treatment time was 30 s. Previous reports on the low pressure plasma treatments showed that, when N_2 plasma was used, even though the surface of CNTs was damaged by ion bombardment, due to the nitrogen doping into multi-walled CNTs, the field emission characteristics were improved [15,23,24]. Therefore, in this study, for the plasma treatment, N_2 was used to remove the residue and to enhance the field emission characteristics of CNTs in addition to He which is used to ignite and sustain stable plasma at the atmospheric pressure. As shown Fig. 2(a), when CNTs were screen printed, due to the organic binder mixed with CNTs, the CNTs could not be seen on the top of the paste in the micrograph even after the firing. However, as shown in Fig. 2(b), after the plasma treatment, about 2 ~ 3 μm thick organic binder material was removed and also the CNTs were exposed on the top of the paste.

Fig. 3 shows the field emission electrical characteristics and field emission images of the CNTs before/after the plasma treatment shown in Fig. 2. Fig. 3(a) and (c) shows those before the treatment and Fig. 3(b) and (d) shows those after the treatment. In Fig. 3(b), the electrical characteristic of the CNTs after the plasma treatment for 10 s was also included. The shape of the field emission curve shown in Fig. 3(a) and (b) appears to be somewhat irregular. In fact, the emission current of screen-printed CNT emitters is initially unstable due to the non-uniformity of the distance between emitter tips and electrode by the existence of both long CNTs and short CNTs. The measurements were made several times repeatedly to remove hot spots caused by long CNTs and the field emission curves obtained in Fig. 3(a) and (b) are the data obtained after 7th measurement. Even though some irregularity is still remained due to the multiple stages of field emission, the initial emission from long CNTs and from shorter CNTs at higher electric fields, more stable and reliable field emission curves could be obtained. As shown in Fig. 3(a), the turn-on electric field, defined as the electric field at 1 μA/cm^2 of the emission current density, was 3.13 V/μm. Also,

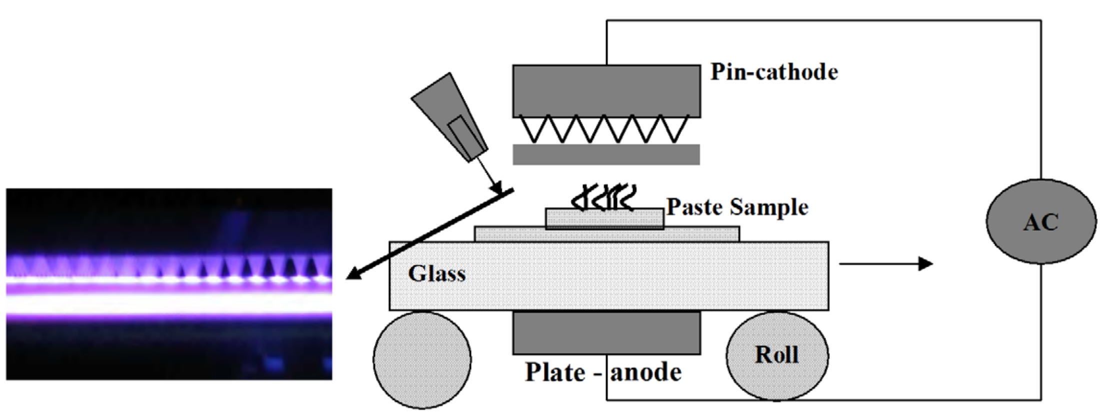

Fig. 1. The schematic diagram of the atmospheric pressure plasma system used in this study.

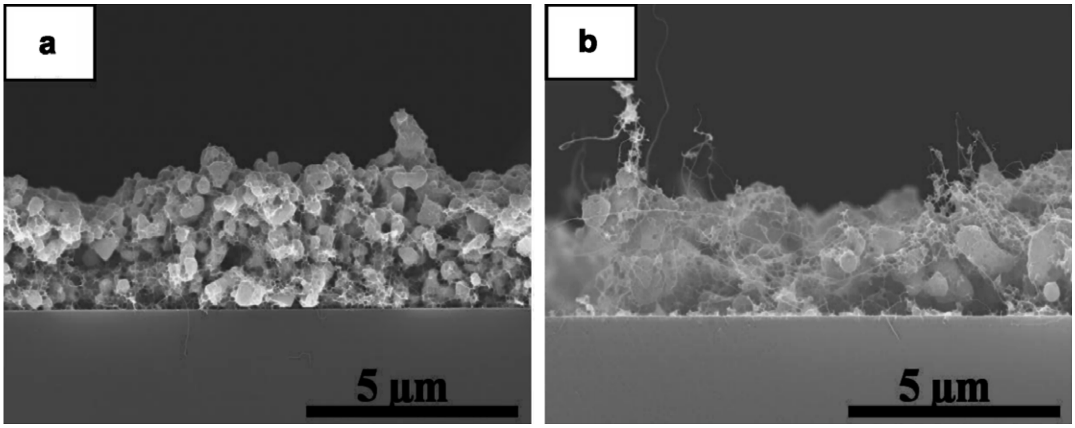

Fig. 2. SEM images of screen printed CNT sample (a) before (b) after He/N_2 plasma treatment for 30 s.

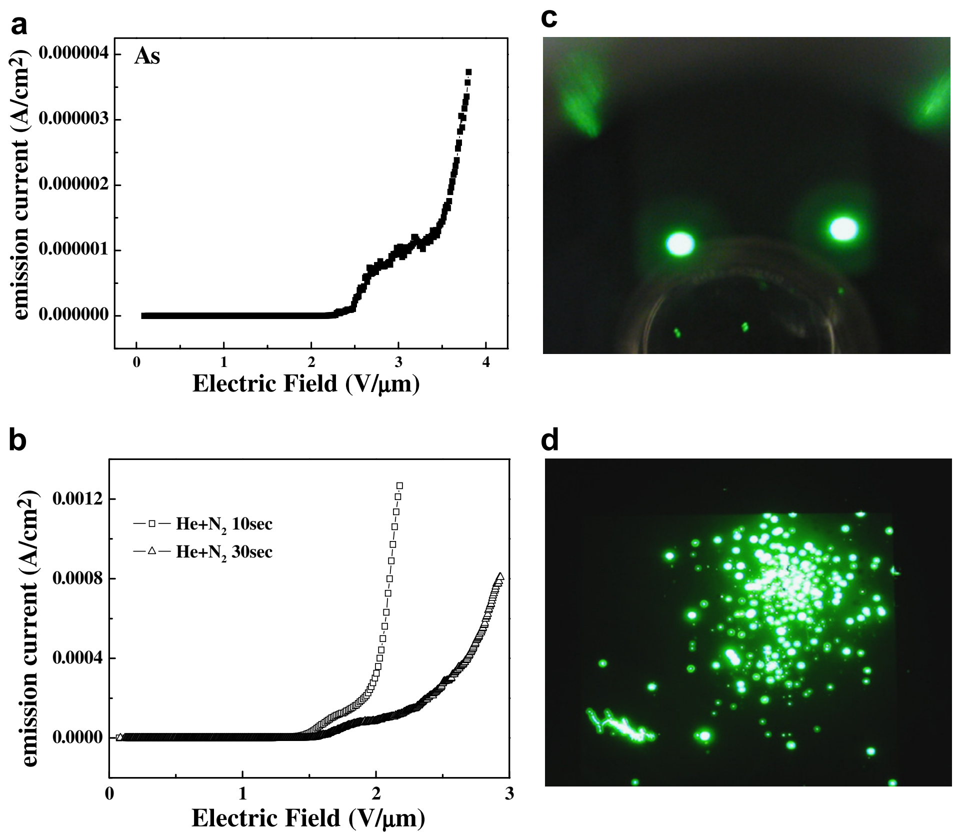

Fig. 3. Emission current density versus electric field for CNTs (a) before and (b) after the He/N_2 plasma treatment for 10 s and 30 s. Field emission image from the CNTs (c) before and (d) after the He/N_2 plasma treatment for 30 s.

as shown in Fig. 3(c), due to the lack of CNTs on the top of the paste, only a few emission sites were observed when 1500 V of voltage was applied. When the CNT paste was plasma treated for 10 s and 30 s using He(10 slm)/N_2(0.1 slm), as shown in Fig. 3(c), the turn-on electric field was decreased to 1.49 V/μm after the treatment for 30 s and was further decreased to 1.21 V/μm when the treatment time was decreased to 10 s. The emission current of the screen printed CNT was lower than a few μA/cm^2 even at 4 V/μm, however, after the 30 s treatment, the emission current was increased (0.8 mA/cm^2 at 2.8 V/μm) and, after the 10 s treatment, it was increased further (1.2 mA/cm^2 at 2.2 V/μm). Also, as shown in Fig. 3(d), after the treatment for 30 s, the increase of emission sites could be observed.

The improvement of field emission characteristics and the increase of emission sites after the plasma treatment are due to the CNTs exposed on the top of organic paste after the treatment as shown in Fig. 2(b) and similar effects have been also observed using low pressure plasmas by other researchers. Kanazawa et al. reported the improvement of field emission characteristics by dissociating CNT bundles and by forming dangling bond on the tip of the CNTs using Ar plasma [25]. Kim et al. also reported the improvement of field emission uniformity through the removal of the paste and by aligning the CNTs by ion bombardment [13]. Therefore, by using the atmospheric pressure plasma treatment, the improvement of field emission characteristics could be obtained similar to those by low pressure plasma treatment. However, as shown by the field emission image in Fig. 3(d), the plasma treatment of CNT paste alone was not enough in removing the CNT organic binder without damaging the CNTs and in aligning CNTs vertically, therefore, obtaining high emission currents at a low electric field and uniform emission sites were difficult.

The best technique known today in removing the organic binder and in aligning CNTs is the adhesive tape technique. As Vink et al. reported, when the organic binder was removed by the tape, the CNTs were vertically aligned due to the vertical force acting on the substrate during the removal of tape [12]. However, organic residues were still remained near the CNT tips after the tape activation and the length of the exposed CNTs was irregular, therefore, uniform emission sites could not be warranted with the adhesive tape technique alone. Therefore, in this study, the tape activated CNTs were also treated by the atmospheric pressure plasma.

Fig. 4(a) and (b) shows the SEM images after the CNT surface treatment using the adhesive tape method and after the surface treatment of the tape activated CNT further by an atmospheric pressure plasma, respectively. The tape activated CNTs were treated by the plasma for 10 s. As shown in Fig. 4(a), after the tape activation, the thickness of the organic binder was decreased to 2 μm compared to 4 μm before the tape activation shown in Fig. 2(a). Also, CNTs were exposed on the top of the organic binder and some of them were vertically aligned. But, as shown in the figure, the length of the CNTs was not even. It is known that uneven CNTs can cause a hot spot effect at the long CNT tips due to the excessive emission and also can result in the decrease of lifetime [13]. Therefore, the CNTs treated by the tape activation were further treated by the atmospheric pressure plasma. As shown in Fig. 4(b), by treating the CNTs further by the atmospheric pressure plasma, the long CNTs appeared to be removed by the plasma treatment.

The tips of the CNTs before/after the plasma treatment were also observed by TEM and the TEM images before/after the atmospheric pressure plasma treatment for 10 s are shown in Fig. 5(a) and (b), respectively. As shown in Fig. 5(a), the CNTs before the plasma treatment were multi-walled CNTs composed of 5 nm of inner diameter, $10 \sim 15$ nm of outer diameter, and $10 \sim 15$ graphite layers with closed CNT tips. However, as shown in Fig. 5(b), after the plasma treatment for 10 s, open CNT tips were formed by cutting off and the crystallinity of the edge and top of the long CNTs was decreased significantly similar to that of CNTs observed after the treatment by low pressure plasma, oxygen, etc [26–29]. The tip of long CNTs was appeared to be attacked more by ion bombardment and was cut-off during the plasma treatment due to the higher electric field formed on the long CNTs compared to the other short CNTs. Therefore, after the plasma treatment, more uniformity in the length of the CNTs could be obtained.

The field emission electric characteristics and the emission images of the tape activated CNTs before/after the plasma treatment shown in Fig. 5 are shown in Fig. 6. As shown in Fig. 6(a), the turn-on field of the tape activated CNT was 0.769 V/μm and that after the plasma treatment was increased to 1.25 V/μm. Also, the electric fields at 1 mA/cm^2 were 1.61 V/μm and 1.95 V/μm for tape activated CNT and for the plasma treated CNT after tape activation, respectively. The increase of turn-on field after the plasma treatment is related not only to the damage of CNTs but also to the removal of long CNTs as shown in

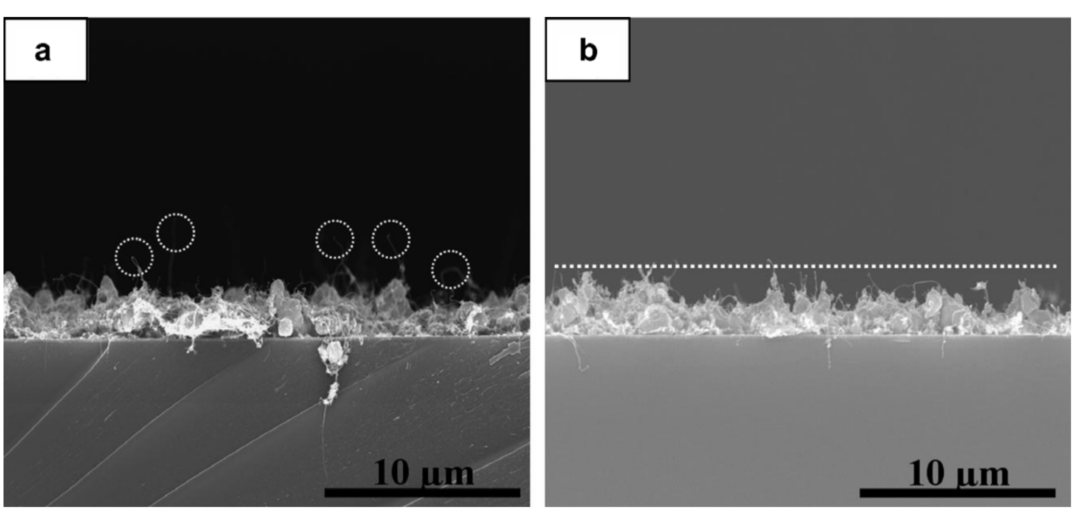

Fig. 4. SEM images of screen printed CNT sample (a) after tape activation and (b) after the He/N_2 plasma treatment for 10 s after the tape activation.

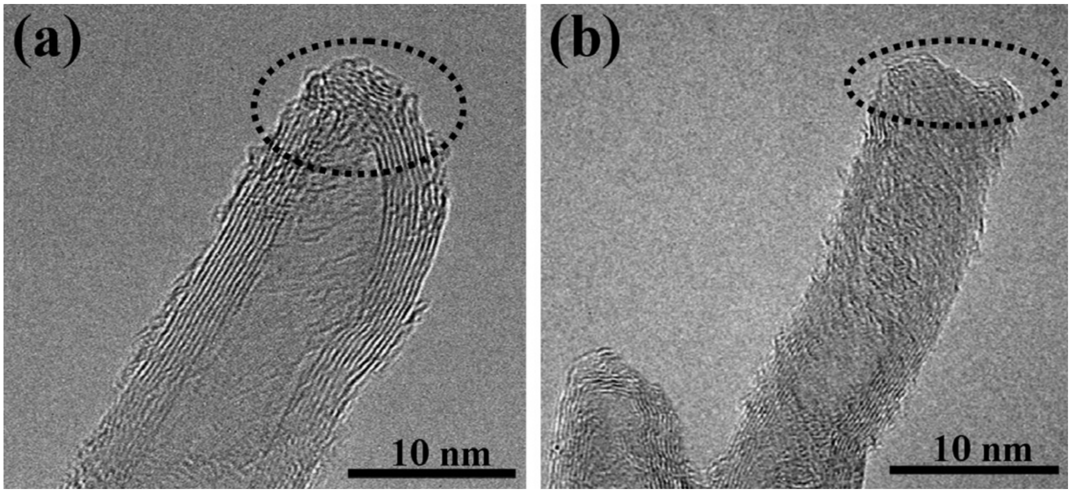

Fig. 5. TEM images of the CNTs (a) before and (b) after the He/N_2 plasma treatment for 10 s.

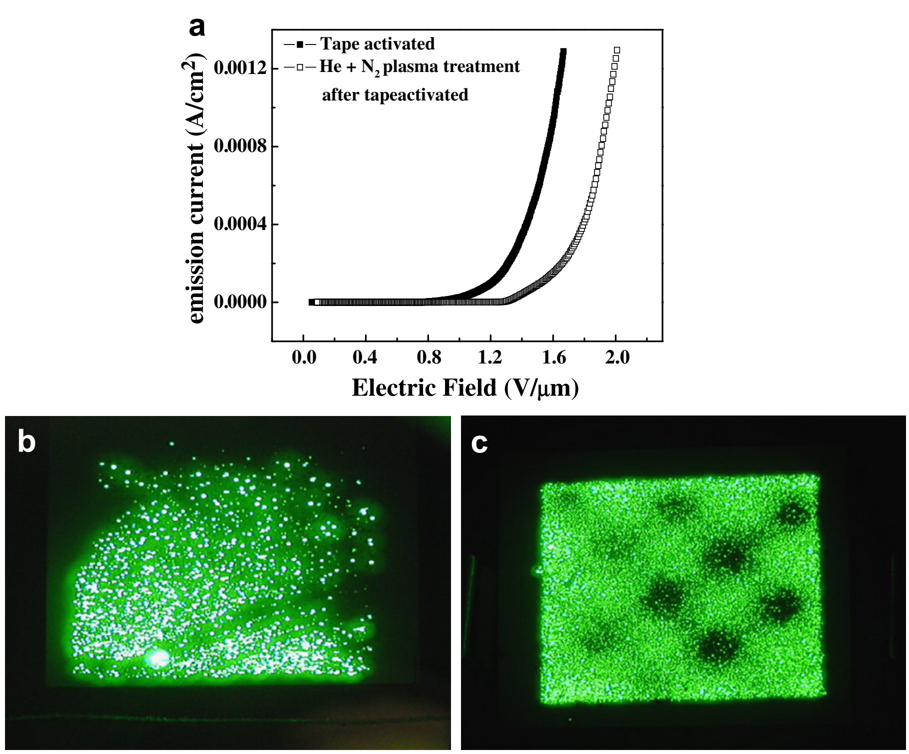

Fig. 6. (a) Field emission characteristics of the tape activated CNTs before and after the He/N_2 plasma treatment for 10 s. Field emission image from the tape activated CNTs (b) before and (c) after the He/N_2 plasma treatment for 10 s.

Fig. 4(b). However, the removal of long CNTs after the plasma treatment resulted in the improvement of emission uniformity. Fig. 6(b) and (c) shows the emission images for the tape activated CNT and for the plasma treated CNT after the tape activation, respectively, at 800 V of applied voltage. In the case of tape activated CNTs, due to the long CNTs existing on the CNT paste, the emission was not dense and uniform because the emission was occurred only at the tip of the long CNTs. However, in the case of the plasma treated CNTs, due to the removal of the long CNTs and also possibly due to the removal of residue on the CNTs remaining after tape activation, denser and more uniform emission could be observed by the increase of emission sites. The dark array image shown in Fig. 6(b) is from the damage of CNTs by the pins of the discharge source obtained without moving the sample. It is believed that, by using the in-line sample moving system, the dark array shown in the figure can be effectively eliminated.

4. Conclusions

In this study, an He/N_2 atmospheric pressure plasma was used as a surface treatment method of screen printed CNT paste and its effects on the field emission characteristics were investigated. The application of He/N_2 atmospheric pressure plasma to the screen printed CNT paste decreased the turn-on electric field from 3.13 V/μm to 1.21 V/μm after the plasma treatment for 10 s and the emission sites were also increased by the exposing the CNTs from the organic CNT paste. When the plasma treatment was applied to the tape activated CNTs, the increase of emission sites could be also observed by the removal of long CNTs and residue on the CNTs formed during the tape activation. It was difficult to replace the tape activation of screen printed CNTs by the atmospheric pressure plasma treatment due to the damage on the CNTs during the plasma treatment for a long period. However, it is believed that the atmospheric pressure plasma treatment can be applied to the surface treatment of the CNT after the tape activation for the improvement of the emission uniformity and lifetime by an in-line process and at a low cost.

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