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Improvement of electron field emission from carbon nanotubes by Ar neutral beam treatment

Se-Jin Kyung[a], *Jae-Beom Park*[a], *Byung-Jae Park*[a], *June-Hee Lee*[a], *Geun-Young Yeom*[a,b,*]

[a]*Department of Advanced Materials Science and Engineering, Sungkyunkwan University, Jangan-Gu, Chunchun-Dong 300, Suwon 440-746, South Korea*

[b]*The National Program for Tera-Level Nano device, Hawolgok-dong, Sungbuk-ku, Seoul 136-791, Korea*

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ABSTRACT

To improve the field emission properties of screen printed carbon nanotube (CNT) films, an Ar neutral beam was used as one of the surface treatment techniques and the CNT field emission characteristics after the treatment were compared with those after Ar ion beam treatment. The Ar neutral beam treatment enhanced the field emission properties of the CNTs and by decreasing the turn-on field and by increasing emission sites. When the field emission properties were measured after the treatment for 10 s with an energy of 100 eV, the turn-on field decreased from 1.7 to 0.9 V/μm while that after the ion beam treatment increased from 1.7 to 2.8 V/μm showing damage of exposed CNTs due to the intensive bombardment by the positive ions in the beam. The neutral beam treatment appeared to expose more CNT field emitters from the CNT paste without cutting or severely damaging the already exposed long CNT emitters because there were no charged particles in the beam.

1. Introduction

For the development of the CNTs as field emitters applied to field emission displays (FEDs), backlight for thin film transistor-liquid crystal display (TFT-LCD) etc., operating voltage and uniformity of the CNTs are the most important factors, and both operating voltage and uniformity of CNTs strongly depend on the length and number of active/aligned emitters per unit area [1,2]. However, in the case of the screen printed CNTs which are widely applied for the development of large size FED or for the TFT-LCD backlight, it is difficult to expose vertically aligned CNTs and is also difficult to control the height uniformity of the emitters and the number of active emission sites per unit area due to the randomness of CNTs involved in the CNT paste during the screen printing [3]. Therefore, to achieve the required characteristics, special surface treatment techniques such as adhesion tape activation, laser treatment, plasma treatment, and soft rubber rolling are often needed [4–8]. However, these methods tend to leave some residue on the exposed CNT surface which can result in non-uniform emission sites. The remaining residue could be further removed by a plasma treatment after the tape activation or soft rubber rolling. However, during the plasma treatment process, long CNT emitters are bombarded intensively by the positive ions due to the high electric field at the long CNT tip, resulting in short length and damaged CNTs [9–13].

Recently, to remove charge related damage during the semiconductor processing, neutral beam etching instead of plasma etching has been developed and, to form an energetic neutral beam, various methods such as reflection of accelerated ions on a plate, charge exchange by the collision between accelerated ions and neutrals, etc. have been used [14,15]. If the neutral beam which is not dependent on the electric field developed near the CNT field emitter is used

* Corresponding author: Address: Department of Advanced Materials Science; Engineering, Sungkyunkwan University, Jangan-Gu, Chunchun-Dong 300, Suwon, 440-746, South Korea. Fax: +82 31 299 6565.
E-mail address: gyyeom@skku.edu (G.-Y. Yeom).

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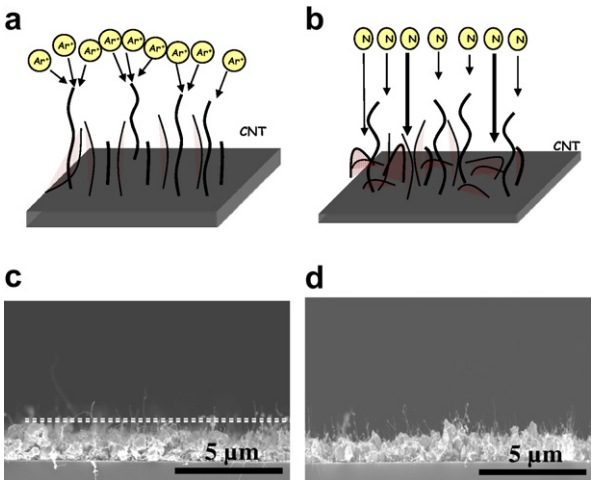

Fig. 1 – Illustration of (a) an ion beam treatment process and (b) a neutral beam treatment process of the CNT emitters, (c) and (d) show the SEM images taken after (c) ion beam treatment for 10 s and after (d) neutral beam treatment for 10 s with the energy of 100 eV.

for the CNT paste treatment instead of conventional plasma treatment involving charged particles, it is believed that it can remove the residue on the CNT surface without significantly damaging the exposed CNTs [8,14–16].

Fig. 1a and b show schematic illustrations of CNT emitters under the treatment expecting during an Ar ion beam treatment and an Ar neutral beam treatment, respectively. In general, after the screen printing and tape activation of the CNT paste, even though vertically aligned CNTs are formed, these CNT emitters tend to have different lengths and non-uniform distribution. If these CNTs are treated by an Ar ion beam, as shown in Fig. 1a, it tends to bombard the long vertically aligned CNTs preferentially which has high field enhancement factor (β) due to the field formation between the bombarding positive ions and the tip of the CNTs. Therefore, the long vertically aligned CNTs are damaged more and shortened by cutting. The long CNTs can induce hot spots during the operation of CNT emitters, therefore, the stability can be improved by removing the long CNTs, and however, due to the damage of the CNT tips and the decrease of CNT length, the turn-on field will be increased. However, as shown in Fig. 1b, if the CNTs are treated by an Ar neutral beam, due to the lack of charge in the beam, the beam bombards the CNTs uniformly not only the long CNTs but also the short CNTs in the bottom of the sample. Therefore, the removal of residue on the CNT surface can be effectively achieved without severely damaging the long CNTs and the decrease of turn-on field. The illustration shown in Fig. 1a and b could be confirmed by observing the CNT emitters by a field emission scanning electron microscope after the treatments by an Ar ion beam (Fig. 1c) and an Ar neutral beam (Fig 1d).

In this study, screen printed CNT paste which was treated using the adhesive tape activation method was further treated using an Ar neutral beam and its characteristics were compared with those of CNTs treated with an Ar ion beam.

2. Experimental

The CNT paste composed of multi-walled carbon nanotubes (MWNT) synthesized by chemical vapor deposition and printed on the active area of $2 \times 2\ cm^2$ of indium tin oxide (ITO) coated soda lime glass substrate was used as the sample. The samples were baked at 120 °C for 10 min in an oven followed by firing at approximately 380 °C under N_2 ambient to remove organic binders, and then naturally cooled down to room temperature. Using an adhesive tape, some layers of the CNT paste were peeled off to expose vertically aligned CNT emitters followed by the treatment by an Ar ion beam or an Ar neutral beam to remove the remaining residue on the CNT surface for the improvement of emission stability, emission current, and uniformity.

The neutral beam source used in this study was composed of an rf ion gun and a planar reflector [16]. The ions were extracted from the ion gun using the grid assembly composed of three grids and were neutralized by reflecting on a planar reflector which is tilted 5° from the ion beam direction. The rf power applied to the ion gun was 200 W with a frequency of 13.56 MHz. The Ar gas flow to the ion gun was 5 sccm and, at this flow rate, the chamber pressure was about 4 mTorr. In the three-grid system, a potential of +10~100 V (V_a) was applied to the 1st grid locate close to the source (acceleration grid), a potential −400 V (V_e) was applied to the 2nd grid (extraction grid), and the 3rd grid located outside of the ground was grounded. The substrate was also grounded. The neutralization efficiency after the reflection of the ions on the reflector was above 99%. Details of the neutral beam source are described elsewhere [14–17]. The Ar neutral beam source was operated also as an Ar ion beam source by removing the reflector of the neutral beam source to understand the effect of charging during the CNT treatment. The operating condition of the Ar ion beam source was the same as that of the Ar neutral beam source. From a previous experiment, it turns out that the energy and flux of the Ar neutral beam are decreased to about 70–80% after the reflection of the Ar ion beam at the reflector [18].

The structural change of the CNTs treated by the beams was observed by a transmission electron microscope (TEM). The emission current and voltage between the electrodes was measured by using the Keithley 2001 multimeter in a vacuum chamber (2×10^{-6} Torr) by increasing the voltage from 0 to 600 V with 2 V intervals. The area of the CNT emitters was $2 \times 2\ cm^2$ and the distance between the anode surface made of indium tin oxide (ITO) coated glass having $5 \times 5\ cm^2$ and substrate surface was 150 μm (the layer thickness composed of remaining CNT/binder on the substrate surface was about 2–3 μm. In addition, the interelectrode distance was kept constant by using a 150 μm spacer). The emission uniformity was also observed by using a green phosphor coated ITO glass as the anode.

3. Results and discussion

Fig. 2 shows the current density (J) vs electric field (E) of the CNT emitters before and after the treatment by the Ar neutral beam and Ar ion beam. To remove initial unstable J–E characteristics caused by various instabilities of the CNT emitter such as the removal of hot spots during the CNT emission,

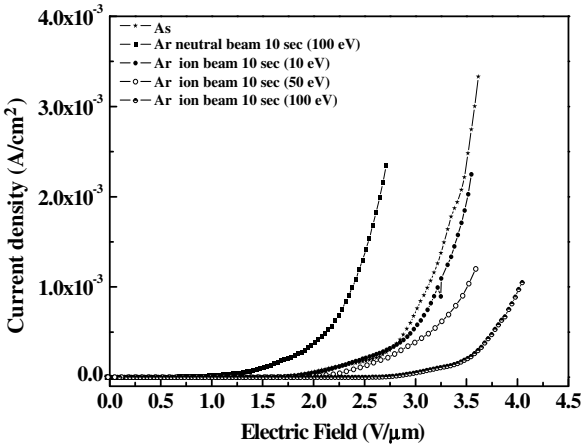

Fig. 2 – Emission current density (*J*) versus electric field (*E*) of the screen printed CNTs treated by different Ar ion beam energies (10–100 eV for 10 s) after the tape activation by adhesive tape. The *J*–*E* curves of the CNTs before and after the Ar neutral beam treatment for 10 s with the energy of 50 eV are also included.

the measurement of *J*–*E* characteristics was repeated several times until it is stabilized, and only the data obtained after the stabilization were included to decrease the measurement error and the results are shown in the Figure. The CNTs were treated for 10 s and, for the Ar ion beam, the acceleration grid voltage was varied from 10 to 100 eV to obtain the ion beam energy about from 10 to 100 eV. The turn-on field (defined as the electric field at 1 μA/cm^2 of the emission current density) of the CNT emitter before the treatment was 1.7 V/μm. And, after the treatment using the Ar ion beam with the energy of about 10, 50, and 100 eV, the turn-on field was increased to 1.8, 2.0, and 2.8 V/μm and, when β was estimated, β was decreased from about 2500 to 2200, 1400, and 1100, respectively. For the Ar neutral beam treatment, as shown in the figure, after the treatment with the energy of 50 eV, the turn-on field was decreased to 1.6 V/μm and β was increased to about 2900. Therefore, through the Ar neutral beam treatment, the improvement of the CNT field emission characteristics could be obtained. It is believed that the improvement of the field emission characteristics of the CNT emitter after the Ar neutral beam treatment is from the uniform treatment of CNT surface without damaging the exposed long CNT surface while the increase of turn-on field and the decrease of β with increasing the energy of the Ar ion beam treatment are believed to be from the damage and cutting of the exposed long CNTs as described in Fig. 2.

Fig. 3 shows the TEM image of the CNTs taken (a) before and after the treatments by (b) an Ar ion beam, (c) an Ar neutral beam, and (d) for the variation of the number of damaged layers observed in 30 CNT samples for each condition. The energy of the beams was about 100 eV by using the acceleration voltage of 100 V and the extraction voltage of −400 V at 200 W of rf power. The treatment time was 10 s. As shown in Fig. 3a, before the beam treatment, the inner and outer diameters of the CNTs were 5 nm and 10–15 nm, respectively, and, the number of graphite layers was about 10–15. No significant damage was found on the surface of the CNTs.

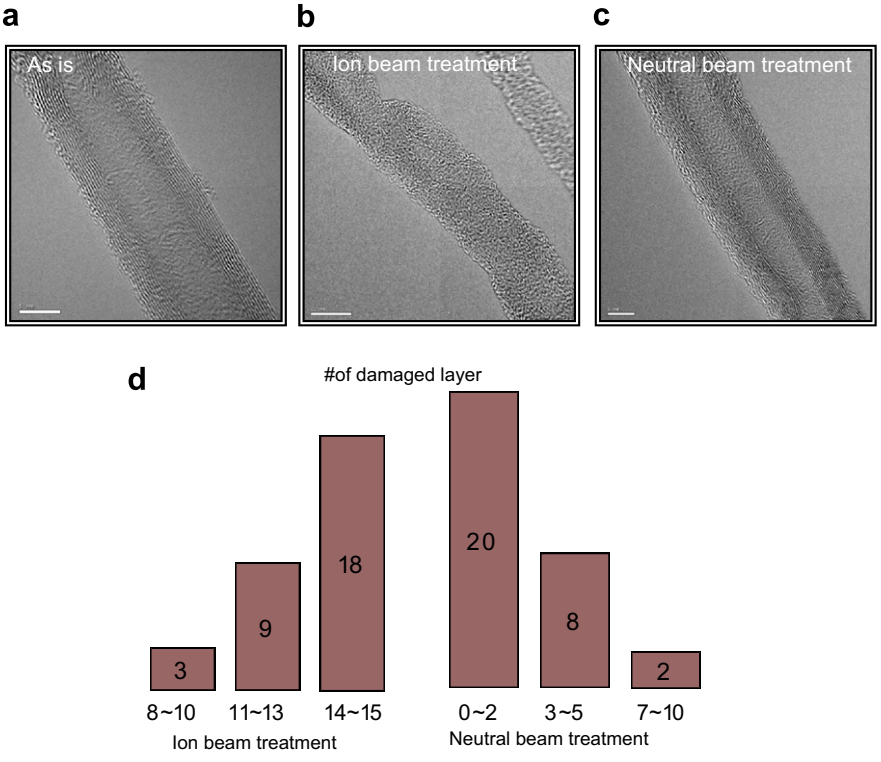

Fig. 3 – shows the TEM image of the CNTs taken (a) before and after the treatments by (b) an Ar ion beam (c) an Ar neutral beam treatment for 10 s with the energy of 100 eV and (d) shows the variation of the number of damaged layers observed in 30 CNT samples for each condition.

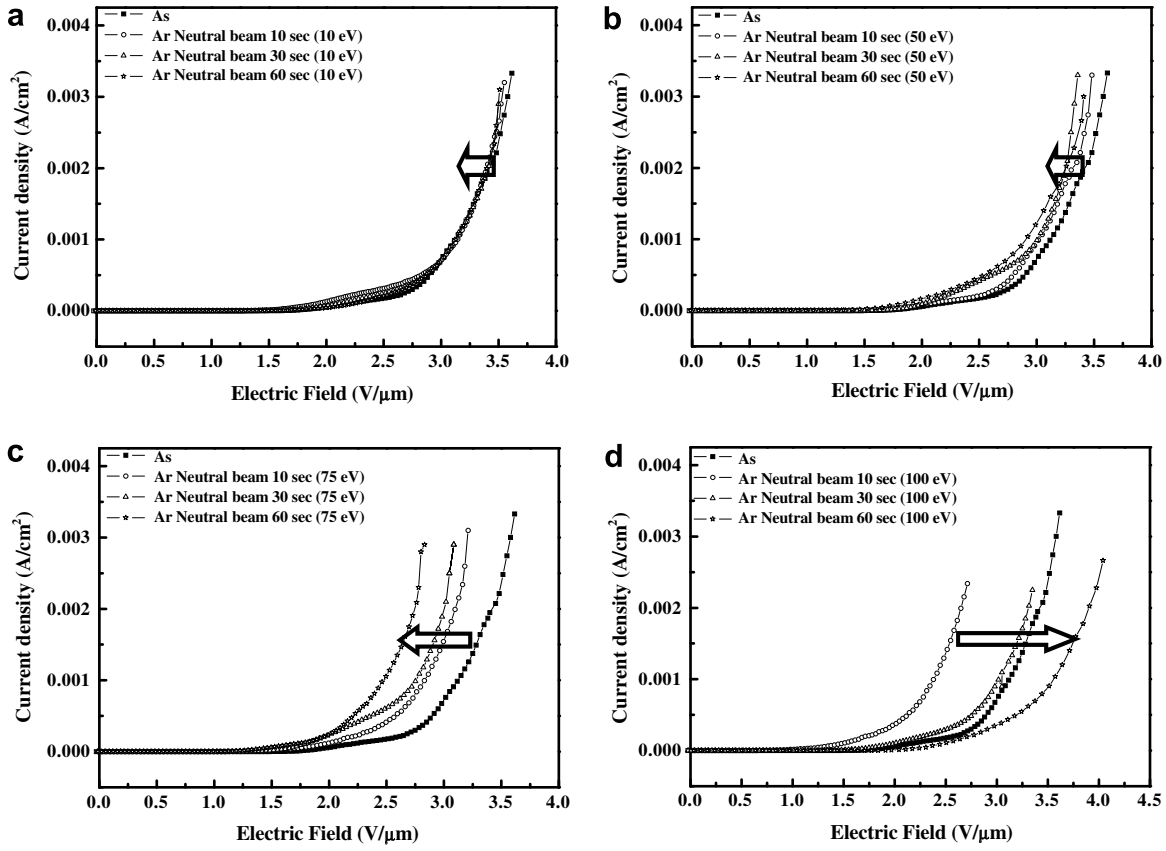

Fig. 4 – Emission current density (*J*) versus the electric field (*E*) of the CNTs treated by the Ar neutral beam for the treatment time of 10–60 s and for the neutral beam energy of (a) 10 eV, (b) 50 eV, (c) 75 eV and (d) 100 eV.

However, as shown in Fig. 3b, after the Ar ion beam treatment, the inner holes were collapsed and the graphite layers were severely damaged and appeared to be amorphous carbon possibly due to the intensive bombardment of the positive ion on the exposed CNTs. Also, as shown in Fig. 3d, after the Ar ion beam treatment, most of the CNT layers were deformed by the ion beam bombardment. This kind of damage to the CNTs was also observed after the plasma treatment, oxygen or ozone treatment, etc. by other researchers [19,20]. However, as shown in Fig. 3c and d, after the Ar neutral beam treatment, only 2 or 5 surface layers of CNT were slightly distorted and no significant damage to the

Table 1 – Turn-on field, the electric field at the current density of 1 mA/cm², and β for the CNTs treated by Ar neutral beams and Ar ion beams

	Energy (eV)	Turn on field (V/μm)	Current density of a 1 mA/cm² (V/μm)	Field enhancement factor (β)
As		1.74	3.14	2523
Ar ion beam 10 s	10	1.77	3.25	2196
	50	1.99	3.52	1426
	100	2.77	4.04	1050
Ar neutral beam 10 s	10	1.648	3.145	2569
Ar neutral beam 30 s		1.636	3.15	2572
Ar neutral beam 60 s		1.656	3.11	2741
Ar neutral beam 10 s	50	1.648	3.048	2887
Ar neutral beam 30 s		1.459	3.036	3047
Ar neutral beam 60 s		1.393	2.92	3484
Ar neutral beam 10 s	75	1.390	2.864	4157
Ar neutral beam 30 s		1.250	2.786	4036
Ar neutral beam 60 s		1.10	2.49	6964
Ar neutral beam 10 s	100	0.940	2.41	8269
Ar neutral beam 30 s		1.548	3.05	2818
Ar neutral beam 60 s		2.04	3.57	1645

CNT surface could be observed possibly due to the uniform bombardment to the sample surface without intensive bombardment to the exposed CNTs.

The uniform bombardment to the sample surface can activate not only the exposed long CNTs but also CNTs located at the bottom of the sample; therefore, more activation can be achieved. Fig. 4 shows the current density (J) vs electric field (E) of the CNT emitters treated by the Ar neutral beam for the treatment time of 10–60 s and for the neutral beam energy of (a) 10 eV, (b) 50 eV, (c) 75 eV, and (d) 100 eV. The summary of the turn-on field, the electric field at the current density of 1 mA/cm^2, and β for the Ar neutral beam treated CNTs in addition to the data of CNTs treated by the Ar ion beam is shown in Table 1. The emission current density (J) can be represented by the following Fowler Nordheim (F–N) equation:

$$J = (AE^2/\Phi)\exp(-B\Phi^{3/2}/E),$$

where, $A = 1.54\times10^{-6}$ AeVV^{-2}, $B = 6.83\times10^{9}$ eV$^{-3/2}$ Vm^{-1}, Φ = 5.0 eV, and E is the local field at the emitting tip [$E = \beta E_0 = \beta(V/d)$]. *The* β for the CNT emitters was calculated from the above assumptions and the slopes were obtained from the F–N plots shown in Fig. 5 which was obtained by replotting Fig. 4. For 10 eV and 50 eV, as shown in Table 1 and Fig. 5a and b, possibly due to the small bombardment effect, no significant improvement of turn-on field and β could be observed with increasing bombardment time.

However, for 75 eV, the increase of bombardment time from 10 to 60 s decreased the turn-on field from 1.4 V/μm to 1.1 V/μm and β increased from about 4200 to 7000 possibly due to the enhanced activation. As shown in Fig. 5d and Table 1, when the bombardment energy was increased to 100 eV, the lowest turn-on field of about 1.0 V/μm and the highest β

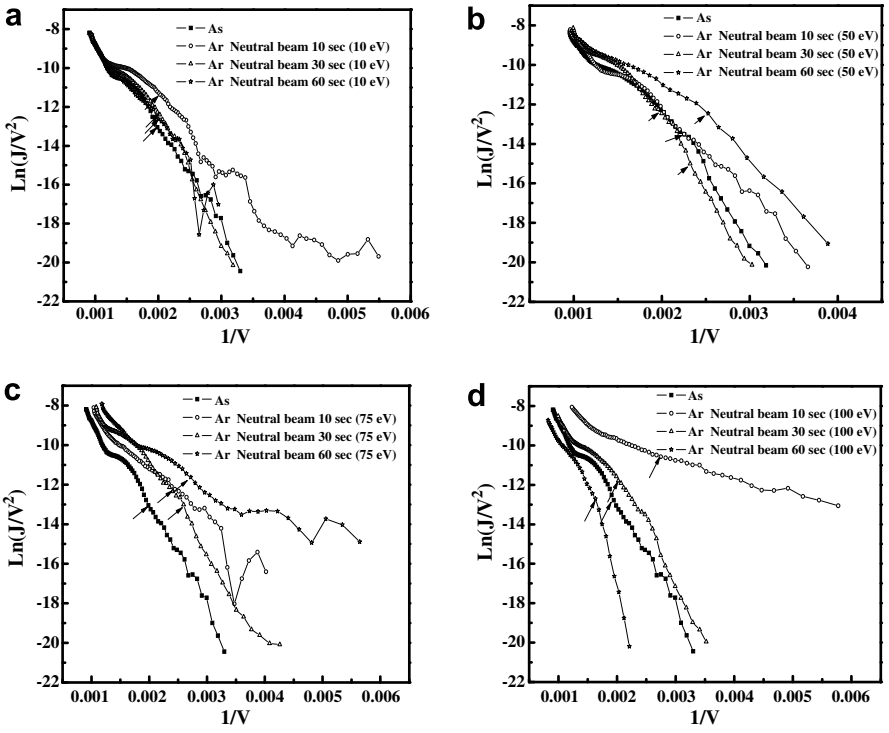

Fig. 5 – Fowler–Nordheim (F–N) plots of Fig. 4. The dots in the curve correspond to the turn-on voltage.

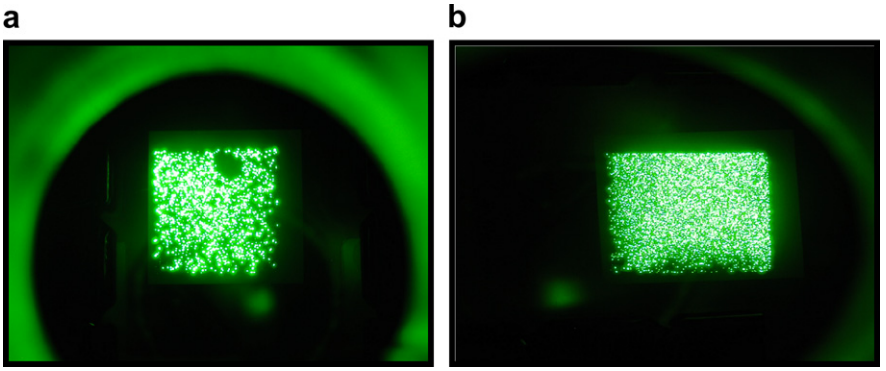

Fig. 6 – Field emission images of the CNT emitters treated by (a) the Ar ion beam and (b) the Ar neutral beam for 10 s with the energy of 100 eV.

of 8300 could be obtained for the bombardment time of 10 s and the further increase of bombardment time increased the turn-on field and β possibly due to the increase of damage on the CNT surface. Therefore, an optimized treatment condition could be obtained by treating the CNT surface for 10 s with 100 eV of Ar neutral beam energy.

Fig. 6 shows the emission images of the CNT emitters treated by (a) the Ar ion beam and (b) the Ar neutral beam for 10 s with the energy of 100 eV. Before the beam treatments, the CNT was screen printed followed by tape activation. As shown in the figure, compared to the CNT treated by the Ar ion beam, the CNT treated by the Ar neutral beam showed the increase of emission sites and more uniform emission sites.

4. Conclusions

In this study, screen printed CNT paste was treated by an Ar neutral beam and an Ar ion beam after the tape activation to remove the residue remaining on the exposed CNT surface and the effect of beam treatments on the morphology and the field emission characteristics of the CNTs was investigated. The treatment by the Ar ion beam for 10 s with the energy from 10–100 eV increased the turn-on field and decreased β due to the intensive bombardment of the exposed long CNT and by damaging the CNT surface severely. However, the treatment by the Ar neutral beam decreased turn-on field and increased β due to the uniform bombardment of Ar beam not only the long CNTs but also the short CNTs in the bottom of the sample, therefore, by activating more CNTs throughout the sample surface. The uniform bombardment to the CNT surface was possible due to the no charge involved in the beam. By the Ar neutral beam treatment for 10 s with the energy of 100 eV, the turn-on field decreased from 1.7 V/μm to 0.9 V/μm and the β increased from about 2500 to 8300.

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