Enhanced field emission and luminescent properties of straightened carbon nanotubes for applications in field emission display

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Abstract

The field emission and luminescent properties of carbon nanotubes (CNTs) that were straightened out by argon ion irradiation were investigated. Argon ion irradiation permanently straightened out both as-grown and screen-printed CNTs in the presence of a strong electric field. The straightening process enhanced the emission properties of CNT films by showing a decrease in turn-on field, an increase in total emission current, and a stable emission. Furthermore, the number of emission sites was confirmed to increase by observing the luminescent properties of CNT films after the straightening. The mechanism involved in the straightening of the CNTs is proposed and the enhancement in field emission is discussed in detail.

1. Introduction

Carbon nanotubes (CNTs) have attracted a great deal of attention as field emitters, because of their high aspect ratio, high mechanical strength, chemical stability, and superior thermal conductance [1-4]. In order to increase the field enhancement factor and improve the emission stability of CNTs, a variety of surface coating treatments have been examined [5-7]. The geometrically controlled growth of CNTs has also been extensively studied in order to optimize and realize their applications in the area of field emission.

The vertical alignment of CNTs is particularly important in applications to field emission displays in achieving a high geometrical enhancement factor β [4,8]. Appropriate vertical alignment can generally be achieved by growing CNTs in densely packed structures, in which case the CNTs grow vertically by van der Waals interactions [4]. It is well known that the mutual shield effect between neighboring CNTs can suppress field emission properties in densely packed CNTs. The maximum field enhancement for inducing the largest emission current density is known to be achieved when the intertube distance is about twice the height of the CNTs [9]. To realize this condition, CNTs must be grown on well-isolated catalyst particles with an optimized distance between the nano-particles. It has recently been reported that well-isolated CNTs can be grown on porous anodic aluminum oxide (AAO)[10] and on Ni dots patterned by e-beam lithography [11,12]. The field emission experiment described in ref. 10 was shown to be consistent with simulation results, in which the intertube distance was related to the height of the CNTs. However, the emission current density was reported to be relatively lower than that of densely packed CNTs reported by other groups [13-15] as well as our experimental results. E-beam lithography is a relatively expensive and low throughput process. In the case of screen-printed CNT films, some protruded CNTs are not aligned vertically and the others are buried under the paste. Therefore, a post process is needed to enhance the field emission properties of CNTs by straightening and to allow the CNTs buried in the binder paste to protrude.

Here, we present an effective method for enhancing the field emission of CNTs. Curly CNTs were grown with a relatively low density followed by a straightening process that involved irradiation by argon ions. Field emission measurements indicated that the emission properties could be significantly improved by straightening out curly CNTs with the

desired low density. This straightening method can also be very effective post-process in improving the geometrical structure of screen-printed CNTs (SP-CNTs). Explanations for the enhancement of emission current and the possible straightening mechanisms of the CNTs are proposed in the next chapters.

2. Experimental

CNTs were produced by dc plasma-enhanced chemical vapor deposition (PECVD) on a Ni sputtered silicon substrate at 450°C. The SP-CNTs films were fabricated by mixing the arc-discharged SWNTs with an organic binder and some additives. The resulting CNT films were irradiated with Ar^+ ions obtained by ionizing Ar gas (at a pressure of 5×10^{-3} Torr) on a cold cathode ion source and accelerating the ions through a potential of 500V.

For field emission measurements, hemispherical tungsten with a 1.0 mm diameter and copper plate were used as the anode electrode, which is designed so as to be movable in the x-y-z directions. The spacing between the cathode and the anode electrodes was maintained at about 200 μm. Field emission measurements were carried out in vacuum with a background pressure of ~ 3×10^{-8} Torr at room temperature. Extended electrical aging was performed to prevent a threshold voltage shift and a change in emission current. I-V measurements were automatically controlled by a computer, which used in-house prepared software. Scanning electron microscopy (SEM), Raman, field emission and the luminescent properties of the prepared CNT films were measured for comparison before and after the straightening of the CNTs.

3. Results and discussion

Figure 1 shows scanning electron microscopy (SEM) images of CNT samples before and after irradiation with Ar ions. Two types of as-grown CNT samples were prepared as shown in Fig. 1(a) and (c). Fig. 1(a) shows curly CNTs, which are oriented in random directions with a relatively low density. The CNT samples shown in Fig 1(c) have two different morphologies, one for a well-aligned short phase CNT and the other one for a long thin phase CNT. We previously investigated the selective growth of these two phases by varying the growth conditions and observed different field emission behaviors for those two CNT phases. Well-aligned short phase CNTs without any long thin phase CNTs were shown to have a relatively high turn-on field of about 11-15 V/μm compared to densely packed CNTs or CNTs mixed with two phases. This result can be due to the relatively large radius of the end tip and low aspect ratio of short CNTs, as shown in Fig. 1(c).

The end stems of as-grown CNTs and SP-CNTs with arbitrary bent complex structures were found to have straightened out permanently after irradiation with Ar ions as shown in Fig. 1(b), (d) and (f). CNTs with a low density, which usually have very curly trunks in as-grown samples, were shown to be positioned erect and normal to the surface after the application of this method. Straightened CNTs with a low density and with mixed phases are shown in Fig. 1(b) and (d) respectively. In the case of screen-printed CNTs, buried CNTs protruded out of the binder paste in addition to the straightening effect without any substrate damage as shown in Fig 1(f).

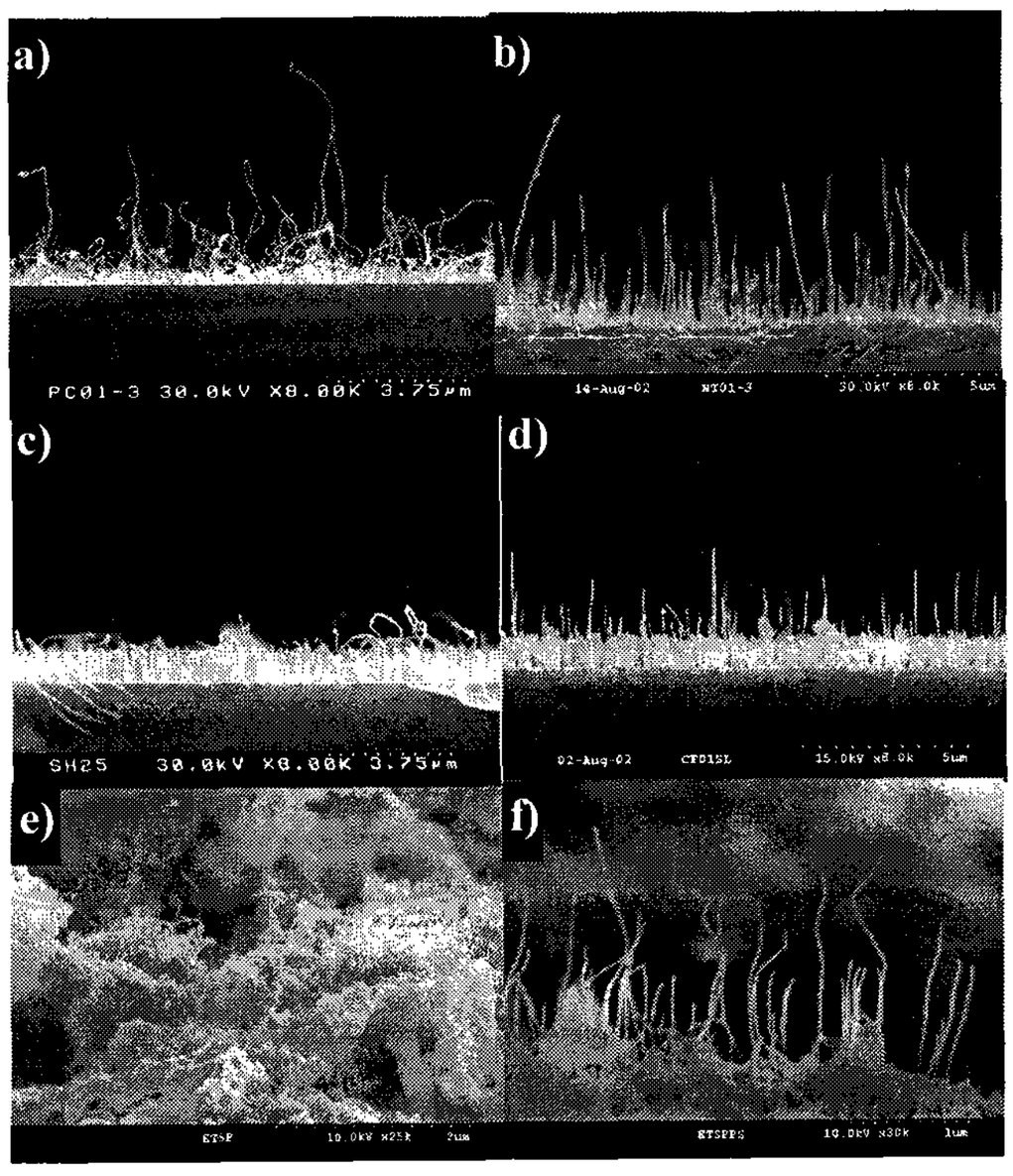


Figure 1. SEM images of CNTs: (a), (c) before and (b), (d) after the straightening as-grown curly carbon nanotubes with low density. SEM images: (e) before and (f) after the straightening the SP-CNT sample.

Recently, Wei, et al.[16] reported that CNTs can be temporarily straightened under an electric field and

are irreversibly deformed during the field emission process. However, the permanent straightening of CNTs was not significantly observed in SEM images even after extracting a high emission current of over 40mA/cm^2. Meanwhile, in our experiments, nearly all of the curly CNTs were straightened after irradiation with argon ions for 10 sec in the presence of an electric field ~10^3 V/cm. The permanent straightening of curly CNTs can be attributed to the combination of the electric field and the charging effect of CNTs as a result of the Ar^+ ions bombardment. The deformation of curly CNTs by Ar^+ ion irradiation may play an effective role in achieving easier flexing and a permanent straightening of curly CNTs. Electro-chemical responses between two nanotubes and between two SWNT sheets have been reported based on the charging effects of CNTs [17,18]. Meanwhile, the permanent straightening of individual CNT can be stimulated by a combination of the charging effect and structure deformation by ion irradiation in our experiments. The structural deformation by Ar^+ ions at the bent point of CNTs may assist in the permanent straightening of CNTs. Extensive studies are currently under study to elucidate the straightening mechanism.

Figure 2 shows the emission current plotted against electric field. The turn-on field for the straightened CNTs (Fig. 1(b)) was significantly decreased compared to that of as-grown CNTs (Fig. 1(a)). This enhancement in field emission can be attributed to the reduced mutual shield effect and the increased beta factor of the straightened CNTs. The turn-on field, at which the emission current density reaches 0.1 μA/cm^2, decreased from 5.5V/μm to 2 V/μm after the straightening of curly CNTs with a low density as a result of irradiation by Ar ions.

Ar ion irradiation will increase the number of defect induced emission sites and also would be expected to contribute to the enhanced field emission properties of the Ar treated CNTs. It was recently reported that the field emission of carbon nanotubes could be enhanced by focused ion beam treatment [19] and an Ar plasma treatment [20]. Figure 3 shows Raman spectra obtained for the CNT samples before and after Ar ion treatment. The ratio of the intensity of the D bands at 1340 cm^{-1} to the G bands at 1590 cm^{-1} was increased with increasing the duration of Ar irradiation. The D band in the Raman spectra of CNTs originates from the finite particle size or lattice distortion [21]. The number of defect sites was clearly shown to have increased by increasing the Ar irradiation time. More emission sites were activated on CNT surface as the result of Ar irradiation.

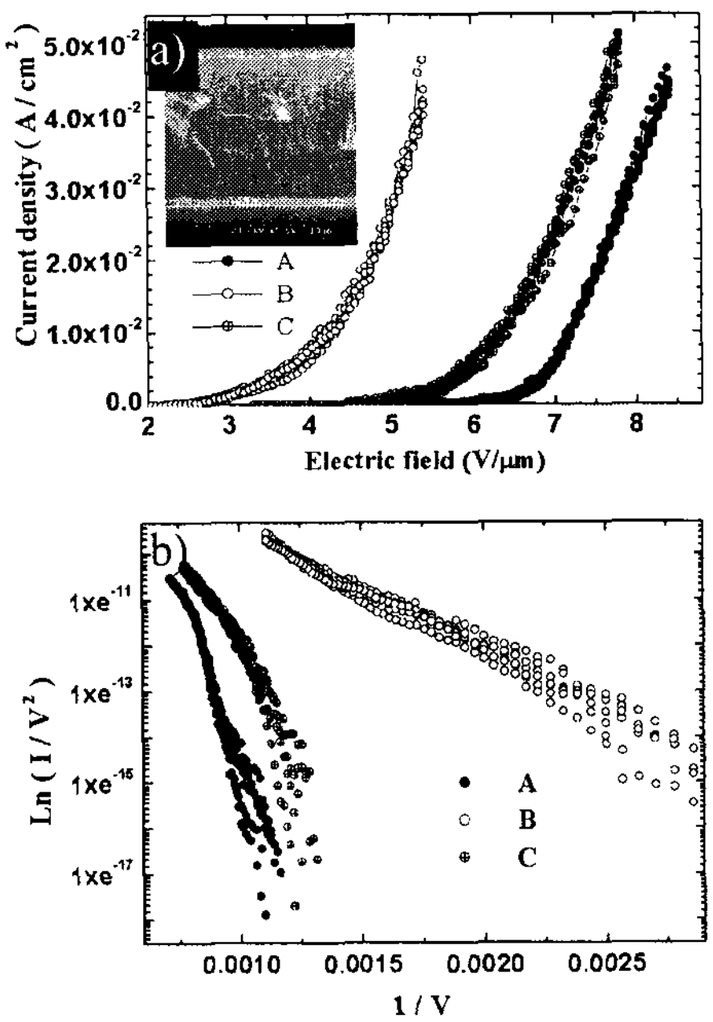


Figure 2. (a) Typical emission current density versus electric field for CNTs before and after the straightening: (A) as-grown curly CNTs with a low density, (B) straightened CNTs and (C) well aligned and densely packed CNTs, which is shown in the inset of the figure. (b) Corresponding Fowler-Nordheim plots for (A) as-grown curly CNTs with a low density, (B) straightened CNTs and (C) well aligned and densely packed CNTs.

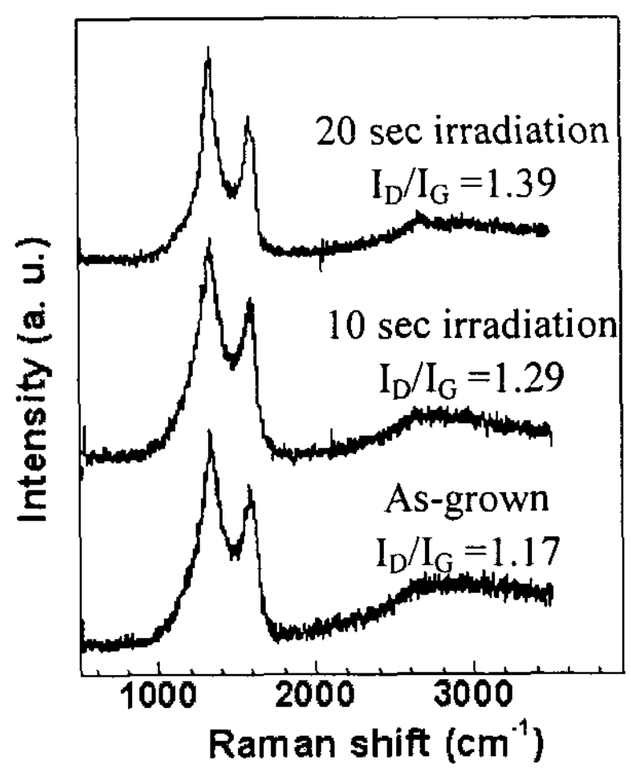


Figure. 3. Raman spectra after different durations of Ar irradiation.

The conventional field emission of electrons can be described by F-N theory [22]. The current density (J), which is related to the local field (E_{loc}) at the emitter surface can be expressed as $J=(AE_{loc}^2/\phi)\exp(-B\phi^{3/2}/E_{loc})$ with $A=1.56\times10^{-10}$ $(A\cdot V^{-2}\cdot eV)$, $B=6.8\times10^9(V/m\ eV^{-3/2})$, with ϕ denoting the work function. E_{loc} is generally related to the macroscopic electric field (E) such as $E_{loc} = \beta E = \beta V/d$, where β (the geometric enhancement factor) can be determined from the slope ($-B\phi^{3/2}/\beta$) of an F-N plot.

Geometric enhancement factors (β) can be obtained in the two regimes of F-N plots assuming the work function of the CNTs to be 5 eV, similar to graphite. In case of the curly CNTs, the slopes of the straight lines in the high voltage (H.V.) region and in the low voltage (L.V.) region of Fig. 2 give values for β from 16000 to 18000 and from 6000 to 7000, respectively. F-N plots for the straightened CNTs were obtained from the I-V characteristics and are shown in Fig. 2(b), where the anode voltage was scanned seven times. The field emission from the straightened CNTs successfully follows F-N behavior with a single linear slope in the F-N plot. In the case of the straightened CNTs, the values of β were found to be about 32000-35000, as calculated from the current rising slope in each F-N plot. The calculated values of β for the straightened CNTs were found to be much higher than those of as-grown densely packed CNTs as well as as-grown curly CNTs, which can be attributed to the well-isolated end geometry and the removal of the mutual shield effect by the straightening of the CNTs. The β values of well-aligned and densely packed CNTs (the inset of Fig. 2) were found to be about 24500 in the H.V. region and 17500 in the L.V. region, respectively. The β values of curly CNTs (Fig. 1(a)) were smaller than those of well-aligned and densely packed CNTs (inset of Fig. 2(a)), which can be attributed to the large shield effect by long curly CNTs.

Bonard et al, reported that the most favorable nanotubes for emission were proved to be long with small diameters and well-isolated from other nanotubes that may screen the applied field in the usual large area of measurement. The emission currents from the most favorable sites then follow the noble F-N law [23]. In our experiments, the effective emitting sites could be increased due to the reduced mutual shield effect by straightening out the curly CNTs with low density and the increase in defect induced emission sites.

Figure 4 illustrates the characteristics of emission current versus anode voltage for the SP-CNTs before and after an Ar irradiation treatment. The inset shows the corresponding F-N plots. The turn-on voltages of the SP-CNTs were not significantly changed before and after Ar irradiation compared to those of as-grown samples. Untreated SP-CNTs have often shown a lower turn-on voltage compared to that of Ar-treated SP-CNTs, which was not observed for as-grown CNT samples. This result could be due to the existence of the most favorable emission sites such as vertically aligned long CNTs formed during the screen-printing process in SP-CNTs. However, the emission behavior was quite different before and after Ar irradiation with increasing applied voltage. The current increasing slope against the anode voltage of Ar-treated SP-CNTs is steeper than that of untreated SP-CNTs, which can be attributed to the greater number of CNTs involved in the field emission of Ar-treated SP-CNTs.

In the case of untreated SP-CNTs, the field emission was suppressed in the mid–range of the anode voltage, which appears as a flat region in F-N plots (inset of Fig. 4). However, the emission current increased rapidly after passing the flat region, which is different from field emissions either with a resistive layer or with a contact problem in the CNT cathode. We previously reported on the degradation of field emission in SP-CNTs with a flat F-N region [24].

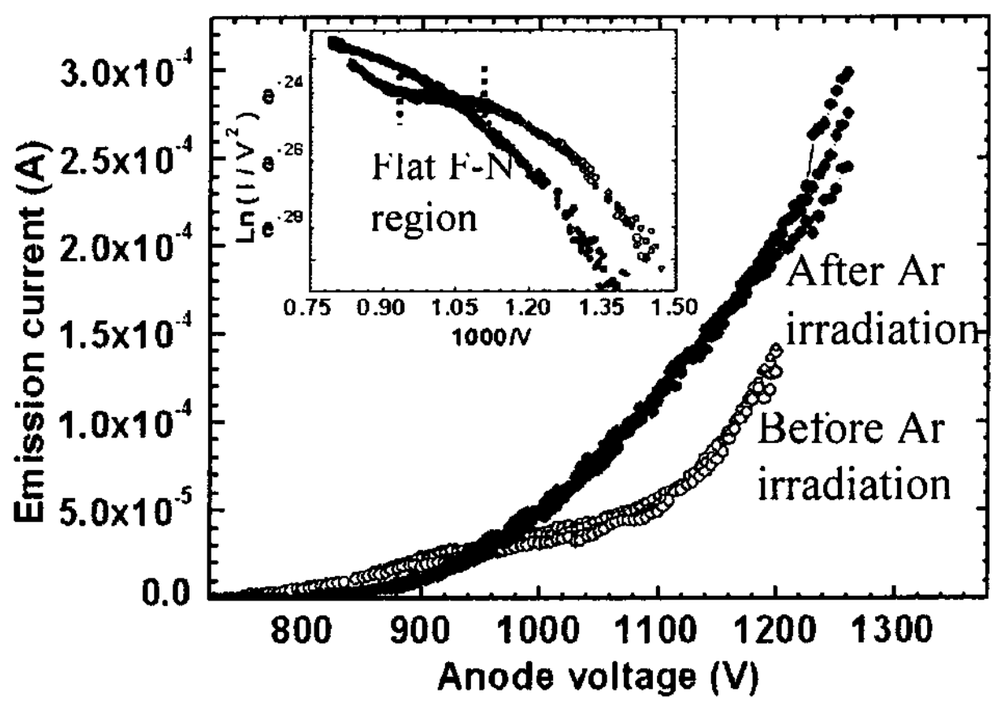
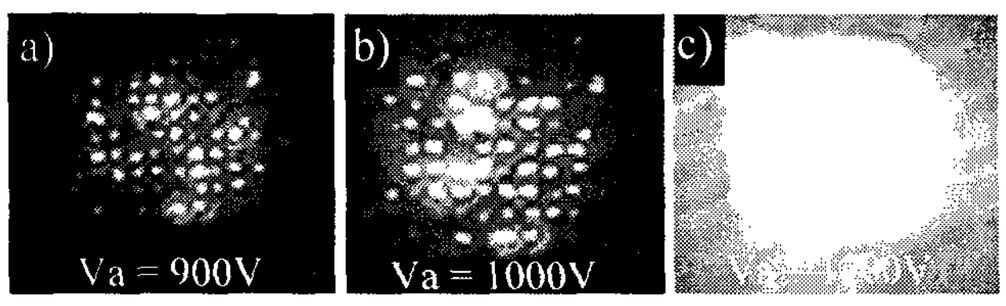


Figure 4. Field emission current versus anode voltage for SP-CNTs (about 100 pixels) before and after the Ar irradiation treatment. The inset shows the corresponding Fowler-Nordheim plots. The spacing between anode and CNTs was maintained at 200 μm.

We experimentally confirmed that this emission behavior is not observed in pristine SWNTs, as-grown MWNTs and Ar-treated CNTs. This novel emission behavior of SP-CNTs can be attributed to the organic binder residue of the screen-printed paste. The Ar irradiation treatment eliminates the flat F-N region of the SP-CNTs as shown in the inset of Fig. 4. This improved emission behavior can be the result of the cleaning process for the Ar irradiation treatment for SP-CNTs.

The ZnS:Cu,Al green phosphor was used to record the emission images of SP-CNTs without pixel patterning before and after Ar ion irradiation, and is shown in figure 5. Emission images were obtained without any aging process in order to compare the initial uniformity in emission. The luminescent pattern of the Ar-treated SP-CNTs emerged to be more uniform than that of the untreated sample. At a relatively lower anode voltage, only a few emission sites were observed for the untreated SP-CNTs compared to Ar-treated SP-CNTs. A few initial hot emission sites (very bright spots shown in Fig. 5(d)) disappeared when the anode voltage was increased to activate the next favorable emitting sites of SP-CNTs. The most favorable emitting site could be activated with the lowest turn-on field and be degraded by the current over the limitation of an individual CNT. The characteristic behavior of the emission current versus the anode voltage can be used to determine emission properties such as the turn-on field and the current density. However, the low turn-on field is not related to the uniform emission of SP-CNTs films. The low turn-on field needs to be verified through an emission study of the triode-type emitter arrays in aspect of a practical driving voltage. The uniformity in emission can be enhanced by the preparation of tuned CNTs preparation and an improved post-treatment.



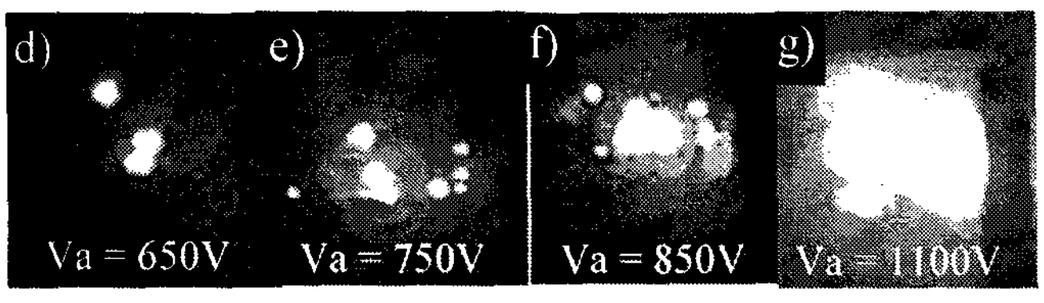


Figure 5. Emission images of SP-CNTs a) – c) with and d) – g) without Ar irradiation treatment. A 300μm-spacer was used.

4. Conclusion

The field emission behaviors of CNT films were investigated with as-grown CNTs and SP-CNTs treated by Ar irradiation. Irradiation by argon ions permanently straightened both as-grown curly CNTs and SP-CNTs that protruded from the buried CNTs. The enhancement in emission properties was clearly the result of the geometrical straightening of CNTs and the increase in the number of effective emission sites on the surface of the CNT films. It was confirmed that the Ar-irradiation treatment improves the uniformity of the field emission and reduces the aging process very effectively. The Ar-irradiation treatment can also play an important role in cleaning the surface of CNT films. In conclusion, an Ar-irradiation treatment is proved to be an effective method for enhancing the field emission properties of CNT films. To achieve further improvement on the spatial uniformity of emission, extensive studies are currently underway, and include the preparation of raw CNT materials with a uniform length and phase, the reduction of paste roughness of the CNT films, and a method for eliminating binder residue on CNTs of the CNT films.

Acknowledgements

This study was performed under Daegu City Government 2002 Nano Project. We would like to thank Dr. Y. -H. Song and Dr. K.-B Kim for the preparation of screen-printed samples.

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