Enhanced Field Emission and Luminescent Properties of Straightened Carbon Nanotubes to be Applied in Field Emission Display

Hyeong-Rag Lee*, Do-Hyung Kim*, Chang-Duk Kim, and Hoon-Sik Jang

Abstract

The field emission and luminescent properties of carbon nanotubes (CNTs) that were straightened by argon ion irradiation were investigated. Argon ion irradiation permanently straightened both as-grown and screen-printed CNTs (SP-CNTs) in the presence of a strong electric field. The straightening process enhanced the emission properties of as-grown CNT films by showing a decrease in turn-on field, an increase in total emission current, and a stable emission. Recurring problems associated with SP-CNTs, such as bent or/and buried CNTs and the degradation in binder-residue-induced emission, were improved by the permanent straightening of CNTs and protruding CNTs from binders by the irradiation treatment, in addition to its surface cleaning effect. Furthermore, we confirmed that the number of emission sites increases by observing the luminescent properties of CNT films after the straightening. These findings here suggest that ion irradiation treatment is an effective method for achieving uniform field emission and to reduce the electrical aging time.

Keywords : carbon nanotube, straightening, enhancement, field emitter displays

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 [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 was 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. Recurring associated with SP-CNTs include bent or/and buried

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CNTs and binder-residue-induced emission degradation. The random geometries of screen-printed CNTs (SP-CNTs) must be vertically straightened, a process that can improve their field emission properties. In addition, a greater number of CNTs can participate in field emission, which reduces the allocated emission current per CNT below the current limitation level, thus permitting the required brightness per pixel for FED applications to be achieved. To this purpose, the mechanical rubbing or lift-up process using a sticky tape can be applied to SP-CNTs. However, undesirable particles or contamination of the CNT surface may be introduced in the FED panel, creating side effects that can result in emission degradation or arc events between the electrodes.

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. An effective method for improving the geometrical structure of SP-CNTs and emission uniformity by an argon ion irradiation treatment is described in this report.

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 500 V. For field emission measurements, hemispherical tungsten with a 1.0 mm diameter and copper plate were used as the anode electrode, which is designed that it can moved in the x-y-z directions. The spacing between the cathode and 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

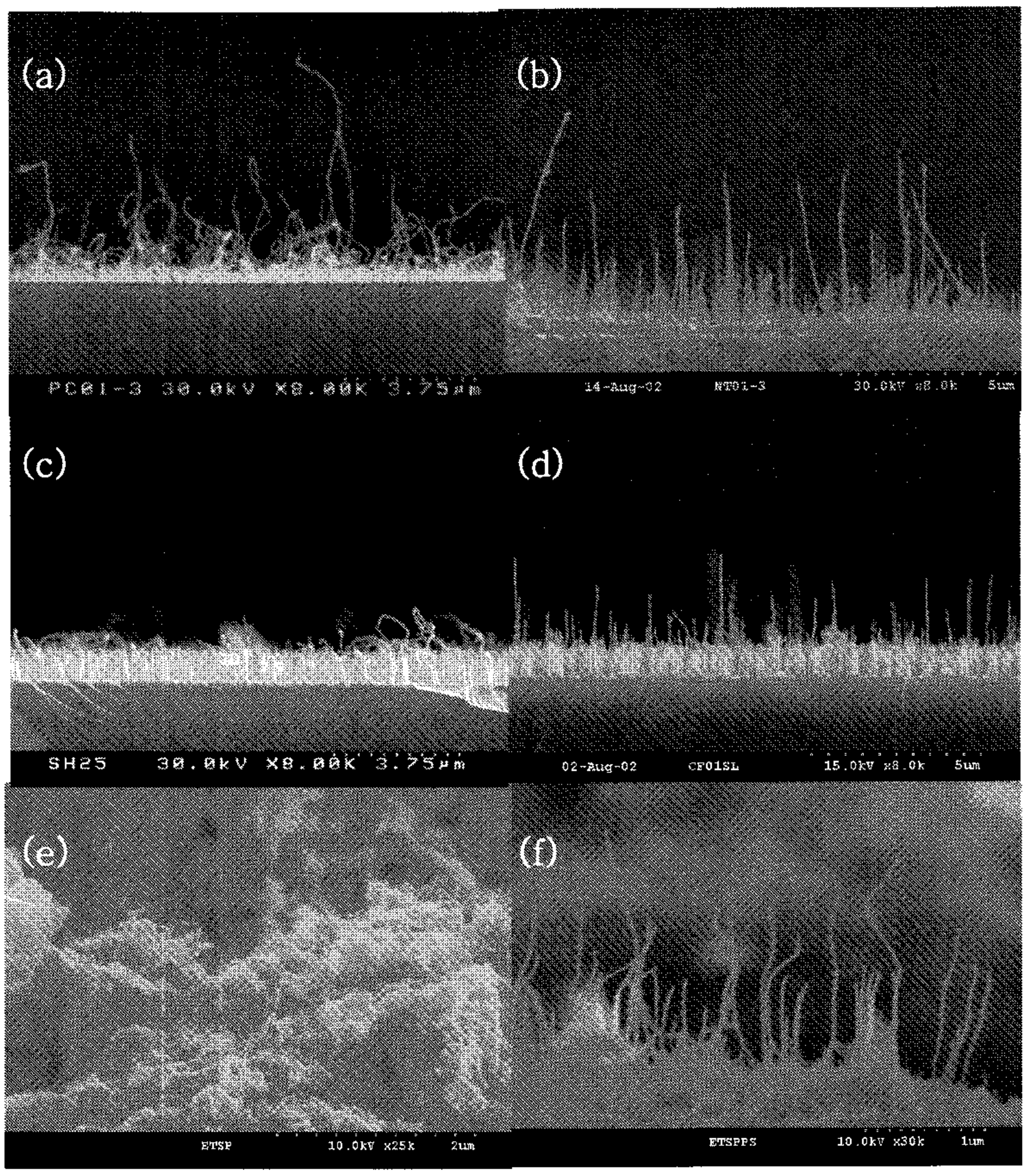

Fig. 1. SEM images of CNTs: (a), (c) before and (b), (d) after the straightening as-grown curly carbon nanotubes with low density. SEM images: (e) before and (f) after the straightening the SP-CNT sample.

performed to prevent a threshold voltage shift and 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

Fig. 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 Figs. 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. Previously we 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 may 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 become straightened permanently after irradiation with Ar ions as shown in Figs. 1(b), (d) and (f). CNTs with a low density, which usually have very curly trunks in as-grown samples, were seen 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 Figs. 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). CNTs was not significantly observed in SEM images even after extracting a high emission current of over 40 mA/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 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 [16,17]. Recently, Wei, et al [18] reported that CNTs can be temporarily straightened by treatment with an electric field of approximately 1.8x10^5 V/cm and become irreversibly deformed during the field emission process, in which the emission current from the nanotube measurd 5.5x10^5 V/cm. The permanent straightening of individual CNTs can be stimulated by thermally induced deformation, as the result of ion irradiation in our experiments. The straightening is likely to be induced at much lower field under ion-irradiation-induced thermal treatment compared to the conditions used in Ref. [18].

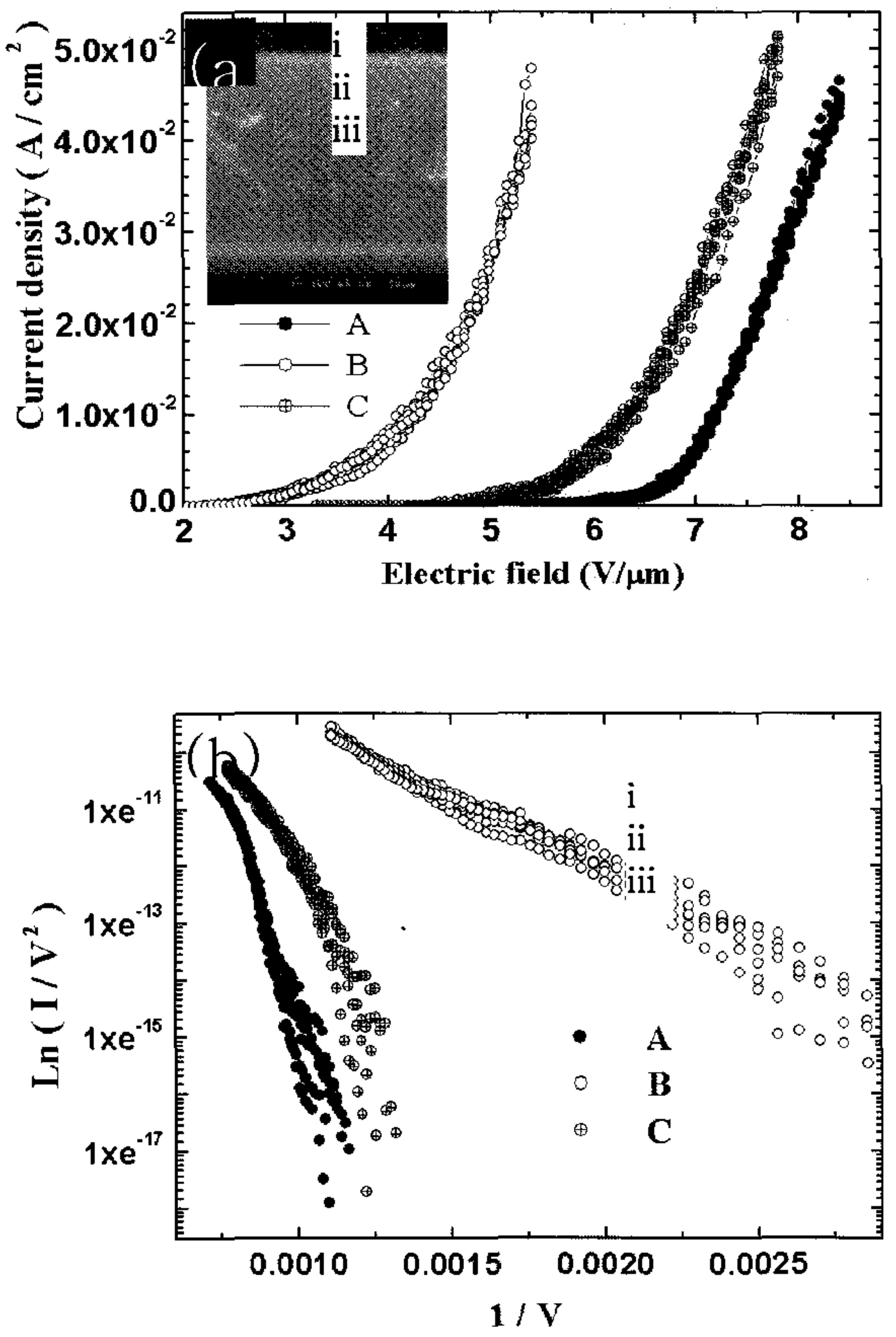

Fig. 2. (a) Typical emission current density versus electric field for CNTs before and after the straightening: (i) as-grown curly CNTs with a low density, (ii) straightened CNTs and (iii) well aligned and densely packed CNTs, which is shown in the inset of the figure. (b) Corresponding Fowler-Nordheim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

Fig. 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 $\mu A/cm^2$, decreased from 5.5 V/μm to 2 V/μm following the straightening of curly CNTs with a low density as a result of irradiation by Ar ions. The conventional field emission of electrons can be described by F-N theory [19]. The current density (J), which is related to the local field (F_{loc}) at the emitter surface can be expressed as $J = \frac{1.5\times10^{-6}}{\phi}\gamma^2(\frac{V}{d})^2\exp(\frac{10.4}{\phi^{1/2}})\times\exp(\frac{-6.44\times10^9\phi^{3/2}}{\gamma V})$, where J denotes units of Acm^{-2} and ϕ the work function in [eV]. F_{loc} [V/m] is the local field at the field emitter surface and is generally related to the applied voltage, such as $F_{loc}=\gamma V/d$, where γ (the field enhancement factor) is dimensionless and can be determined from the slope ($-6.44\times10^9\phi^{3/2}d/\gamma$) of an F-N plot. Geometric enhancement factors (γ) can be obtained in the two regimes of F-N plots assuming the work function of the CNTs to be 5 eV [20], which is 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 average values for γ of about 1800 and 800, respectively. The average γ values of well-aligned and densely packed CNTs (inset of Fig. 2) were found to be about 2000 in the H.V. region and, 700 in the L.V. region, respectively. F-N plots for the straightened CNTs were obtained from the I-V characteristics and are shown in Fig. 2(b). 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 average values of γ were found to be about 4900, as calculated from the current rising slope in each F-N plot. The calculated values of γ for the straightened CNTs were found to be much higher than those of as-grown densely packed CNTs and as-grown curly CNTs. Bonard et al, reported that the most favorable nanotubes for emission were long, with small diameters and well-isolated from other nanotubes that may screen the applied field in the usual large area of measurement [21]. The γ factor can be increased with increasing CNT length by the straightening the long curly CNTs. The γ factor of the diode-type CNTs can be approximated by the formula $\gamma_0 = 1.2(h/r+2.15)^{0.9}$ in the range of $4 \le h/r \le 3000$ [22]. The straightened CNT can increase the aspect ratio (h/r) by increasing the effective vertical length of the CNTs for field emission. The γ factors are increased from about 600 to 4780 with increasing length of the isolated CNT length (h) from 1 μm to 10 μm by the above mentioned calculation, assuming that CNTs have a radius (r) of 10 nm. The γ value (γ =4900) for a straightened CNT, and the vertical length of a CNT after straightening curly CNT would be about 10 μm. However, the lengths of most were found to be below 10 μm, as evidenced by SEM data. If the mutual shield effect is considered, such a high enhancement factor of straightened CNTs would be difficult to achieve. Therefore, an additional factor must be considered for including the high enhancement in field emission of the straightened CNTs prepared here.

Recently, various treatment techniques, such as a hydrogen plasma procedure and ultraviolet laser treatment, have been developed for improving the field emission properties of tip-type CNTs, in which the removal of catalyst particles on the CNT tips was found to be a critical factor in the enhancement of field emission [23,24]. Our CNTs were grown via a "base model" mechanism with Ni particles at the bottom of the CNTs. Thus, the enhanced field emission behavior cannot be said to be attributed to the elimination of catalyst particles on the CNT tips. Therefore, there must be other explanations to explain the observed enhancement in field emission. Ar ion irradiation is be expected to increase the number of defect induced emission sites and is also considered to the enhanced field emission properties of the Ar treated CNTs as well. It was recently reported that the field emission of carbon nanotubes can become enhanced by focused ion beam treatment [25] and Ar plasma treatment [26].

Fig. 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} increased with increasing duration of Ar

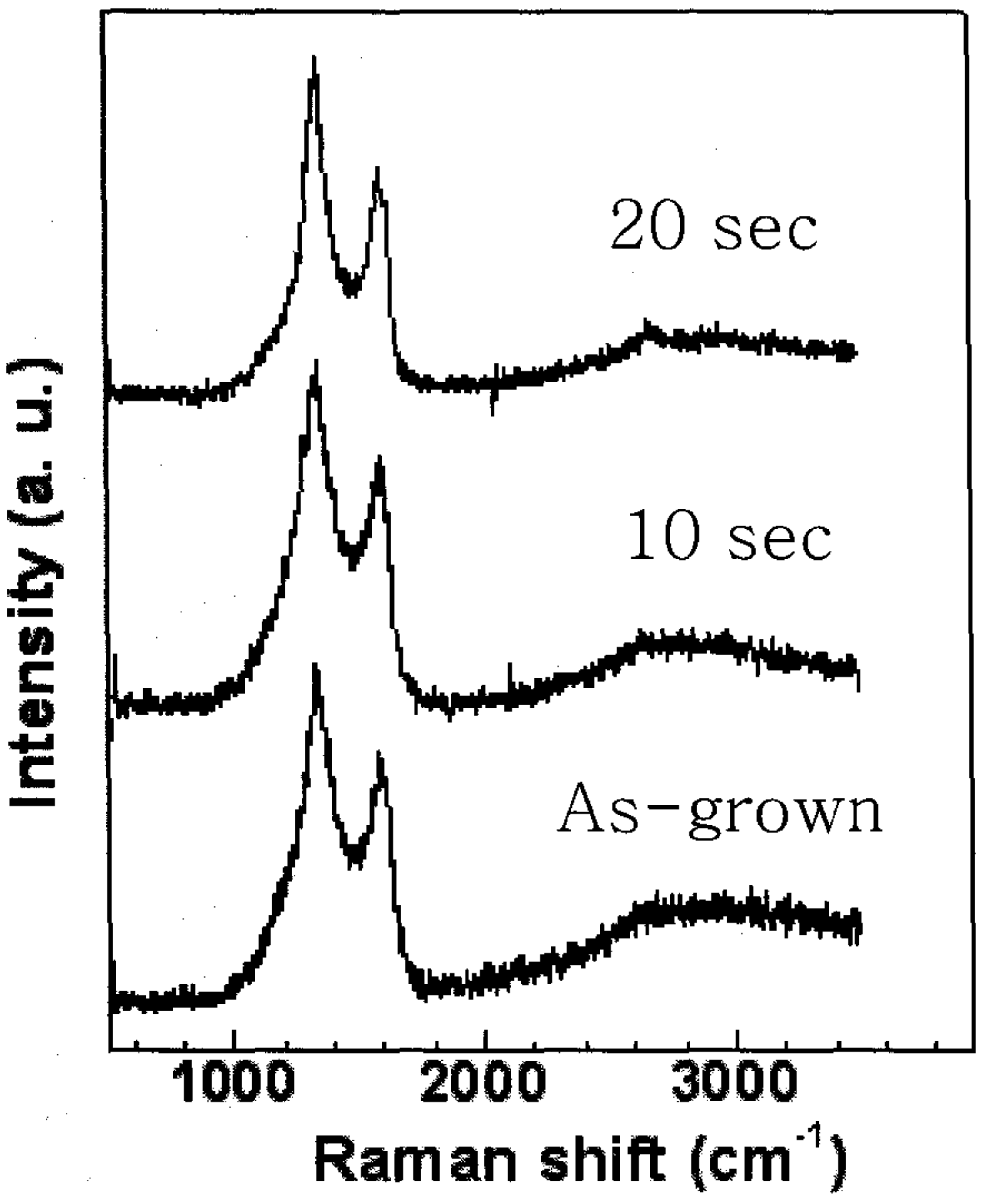

Fig. 3. Raman spectra after different durations of Ar irradiation.

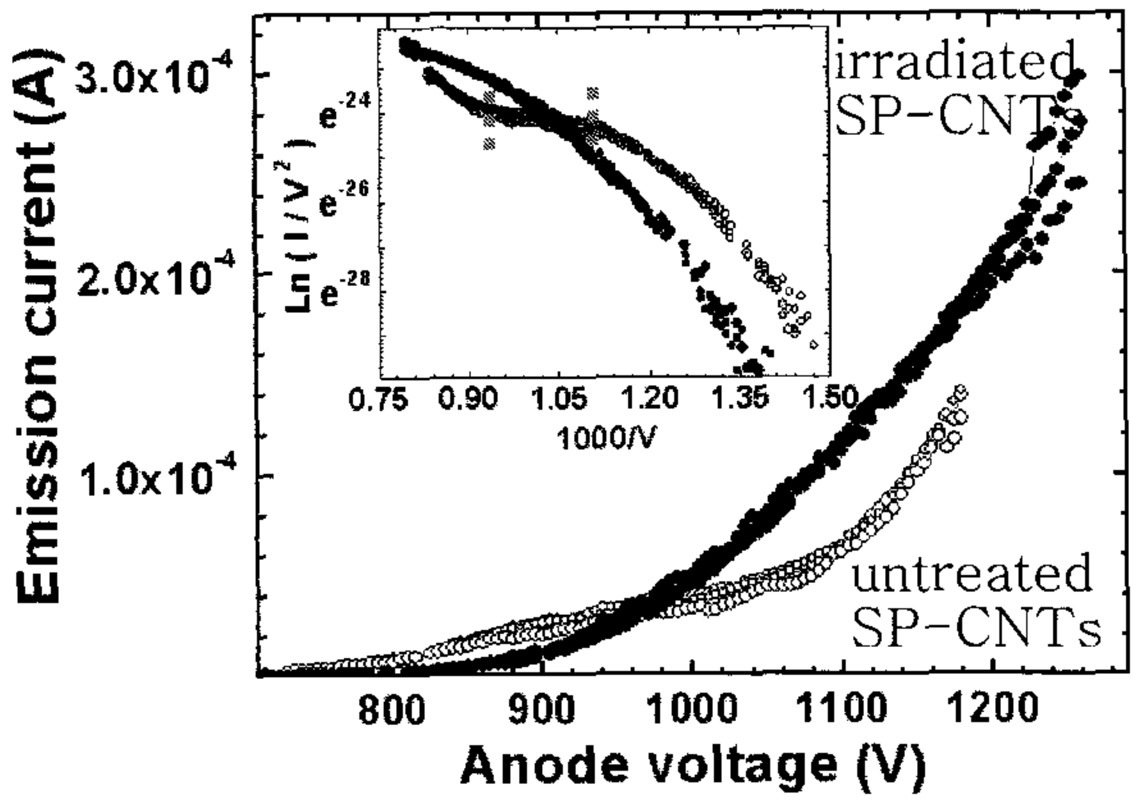

Fig. 4. Field emission current versus anode voltage for SP-CNTs with 100 pixels before and after Ar irradiation treatment. The inset shows the corresponding Fowler-Nordheim plots. The spacing between anode and CNTs was maintained at 300 μm.

irradiation. The D band in the Raman spectra of CNTs is associated with disorder-induced features of graphite [27, 28]. The number of defect sites clearly increases with increasing time of Ar irradiation. Additional emission sites can be activated on the CNT surface as a result of the Ar irradiation. Long straightened CNTs can be more effective under the reduced mutual shield effect that by the straightening of low density CNTs that represents the main difference in the field enhancement factor γ between the straightened and densely packed CNTs in our experiments. To achieve such a high enhancement corresponding to the irradiation-induced straightened CNTs, more effective surfaces of CNTs must assist, in addition to the geometrical straightening effect.

Fig. 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 to 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 was 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 [29]. We have 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 may 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. Furthermore, this improved emission behavior may be the result of the cleaning process for the Ar irradiation treatment for SP-CNTs.

Luminescent patterns were measured, in order to compare the special uniformity of light emission of SP-CNTs before and after Ar ion irradiation using a ZnS:Cu,Al green phosphor, and these data are shown in

Fig 5. Emission images were obtained without any aging process in order to compare the initial uniformity in emission. The luminescent patterns of the Ar-treated SP-CNTs were 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(a)) disappeared when the anode voltage was increase to activate the next most favorable emitting sites of the SP-CNTs. The most favorable emitting site could be activated via the use of lowest turn-on field and was degraded by the current over the limitation of an individual CNT. The characteristic behavior of the emission current versus anode voltage can be used to determine certain 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 the SP-CNTs films. The uniformity in emission can be enhanced by preparing a tuned CNTs and an improved post-treatment.

Distinct local measurements were executed for 10 pixels of the SP-CNTs before and after the irradiation treatment and the corresponding current-voltage data were obtained, as shown in Fig. 6. The pixel was square which is 250 μm×250 μm. The anode probe was maintained at a distance of 300 μm from the CNT pixel. The turn-on field between pixels in the SP-CNTs without ion irradiation treatment showed a large scatter, as shown in Fig. 6(a). This is because some CNTs protrude above the average SP-CNT pixels, and are capable of forming hot spots (Fig. 5a). After a 10sec-irradiation, SP-CNTs showed relatively small deviations in turn-on field between the pixels. A uniform turn-on field distribution can be achieved after the optimum 20-sec irradiation treatment, consistent with the luminescent image in Fig. 5(e)-(g). The turn-on field and uniformity can be improved by the further tuning of the ion dose using a lighter gas ion.

4. Conclusions

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 as-grown CNT films. It was confirmed that the Ar-irradiation treatment improves the uniformity of the field emission and reduces the electrical aging process very effectively. The Ar-irradiation treatment can also play an important role in cleaning the surface of SP-CNT films. To achieve further improvement on the spatial uniformity of emission, extensive studies are currently underway, which 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

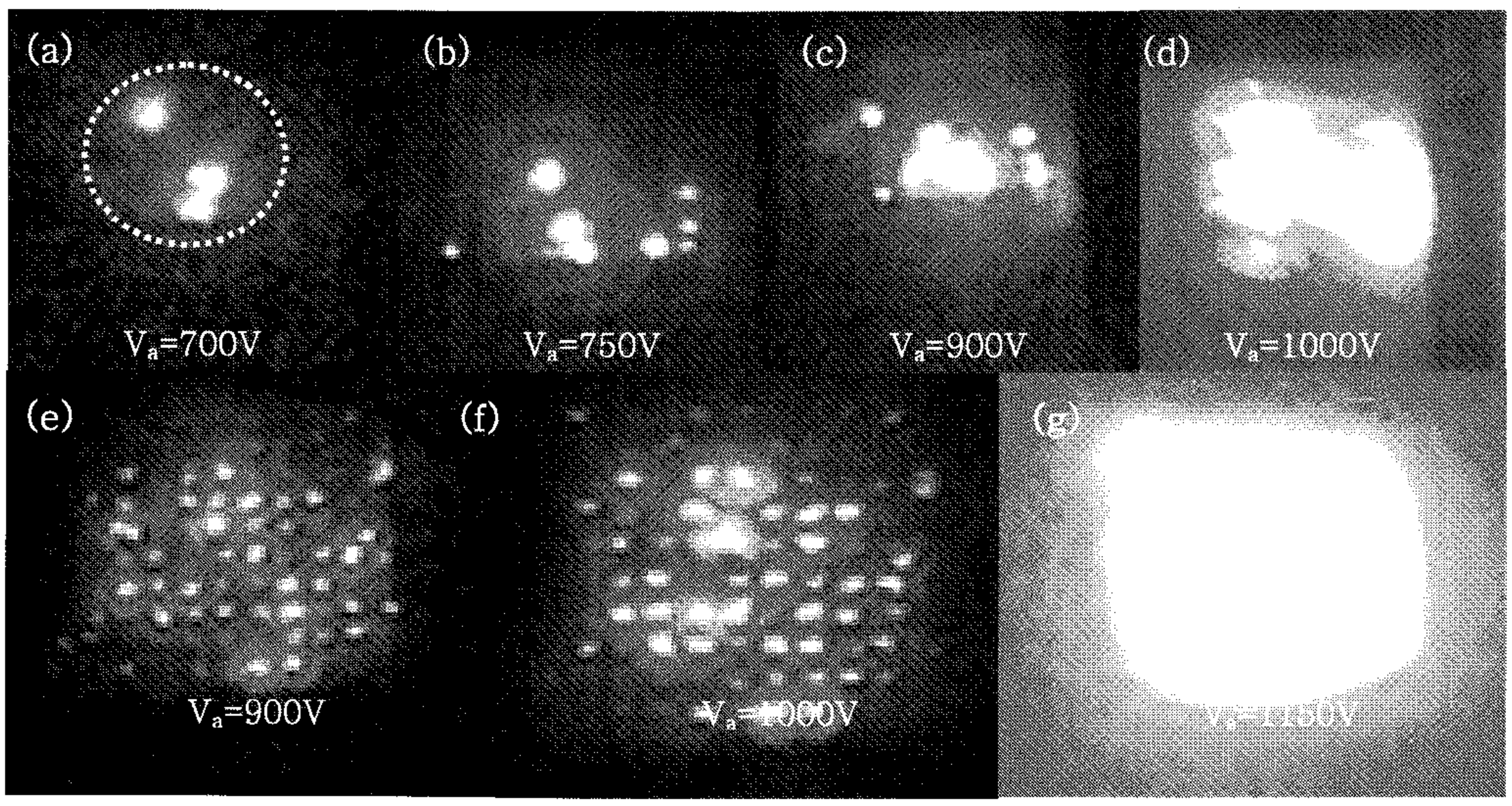

Fig. 5. Emission images of SP-CNTs (a)–(d) without and (e)–(g) with Ar irradiation treatment for 20sec. A 300μm-spacer was used.

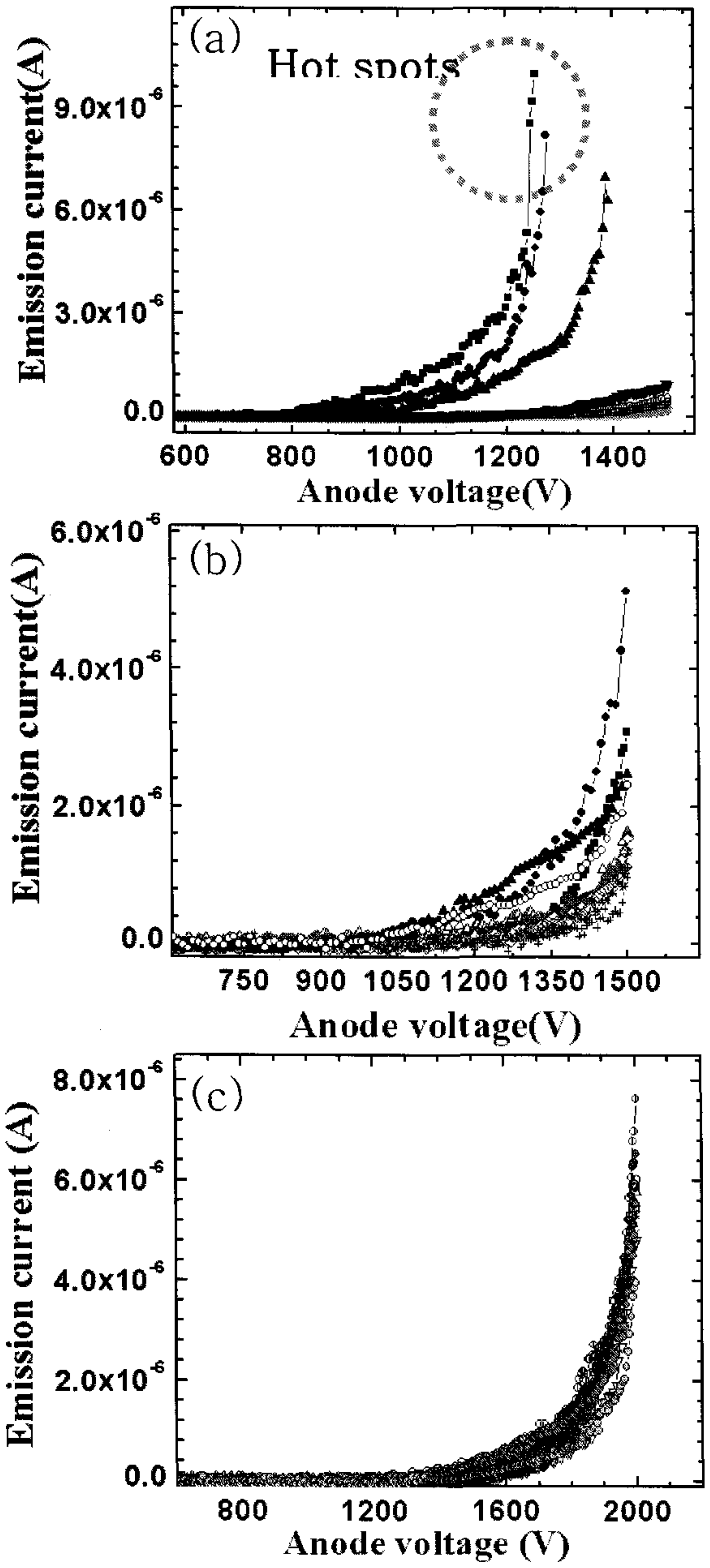

Fig. 6. I-V graphs obtained from the local measurement of the emission current for 10 pixels of SP-CNTs with different ion irradiation times. (a) 0sec; (b) 10sec; and, (c) 20 sec

eliminating binder residue on CNTs of the SP-CNT films.

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