Effect of Current-Aging on Field Emission from Carbon Nanotube Field Emitter Arrays

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Abstract

We studied the effect of current-aging on field emission from carbon nanotubes field emitter arrays (CNT-FEAs) selectively patterned by the resist-assistan tpatterning(RAP) process. After sustaining the electric field when starting emission current density (J_s) is 0.1 mA/cm^2 during 40 hrs, it was observed that the field emission property and uniformity were remarkably improved due to the elimination of oxygen atom and thus the reconstruction of carbon bonding at the tip of CNTs during field emission.

1. Introduction

Carbon nanotube (CNT) has been highlighted as candidates of field-emission emitters and vacuum nanoelectronic devices. Since the discovery of carbon nanotubes, the structural, electrical, mechanical, electromechanical, and chemical properties have been investigated to explore the applications of the materials. The large and stable emission properties are the important factor for application of electron emission tip.

In this study, after sustaining the electric field when starting emission current density is 0.1 mA/cm^2 during 40 hrs in dc-mode, the electron emission property increases almost six times of primitive CNT-FEA.

The transmission electron microscope (TEM) have been used to find out the structural relationship between the CNT-FEAs and the electron emission current. Further, X-ray photoelectron spectroscopy (XPS) has been used to analyze the ratio of carbon and oxygen concentration and their bonding nature before and after the aging treatment.

2. Experimental

The CNT electron emitter array was formed using triode type plasma enhanced chemical vapor deposition (PECVD) process. The CNT growth was performed at 580 ^oC under the pressure of 2.0 Torr in of C_2H_4 and NH_3 mixture with 40:60 ratio respectively. Resist assisted patterning (RAP) process was used to from the CNT electron emitter arrays having 40 μm pitch island.[1,2] The diameter of each island was fixed as 5 μm. The field emission property of the grown CNTs has been carried out using a diode type electron emission measurement system under vacuum (< 1 X 10^{-6} Torr). The distance between the anode and cathode was fixed as 150 μm during the measurement. Current aging was performed with 6.87 V/μm field. The fixed was sustained 40 hrs.

3. Results and discussion

Figure 1 shows the SEM images of the grown CNT electron emitter arrays. The RAP process for selective growth and the uniformity of each island are examined through SEM. The CNT-FEAs can grow on selective position with excellent uniformity and vertically aligned.

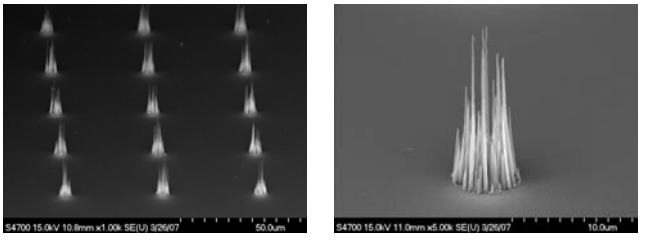


Fig 1. Scanning Electron Microscope images of the CNT electron emitter arrays.

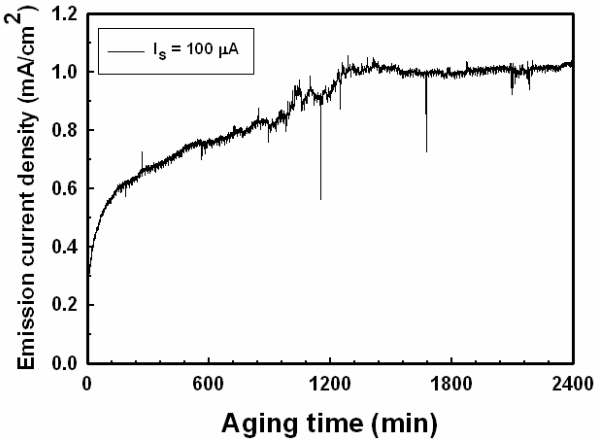


Fig 2. Emission current density with aging times

To obtain very stable electron emission of the CNT-FEAs, the emitter array was aged with constant bias. Figure 2 shows the J–t curves for 40 hr aging times. When the electric field is 6.87 V/μm (J_s= 100μA), the emission current increases initially and then saturated. The stable emission current was about 1.0 mA observed after 1,400 minutes.

Figure 3 shows electron emission characteristics and the Fowler-Nordheim plots with aging treatment. The electron emission current of treated CNT-FEA showed a current density of 1.55 mA/cm^2 at 8 V/μm. This electron emission current is almost six times of primitive CNT-FEA. Further, turn on field decrease from 4.66 V/μm to 3.7 V/μm at 1μA emission current density. The F-N plot indicates the emission current is governed by a tunneling process. The field enhancement factors of CNT-FEAs after aging shows 30,867. For the calculation, the work function of CNT was assumed to be 5.0 eV.

The enhanced electron emission of the emitter array will be related on structural change of CNT emitters. Figure 4 indicates the TEM images of CNT emitter tip. More interestingly, we observed that the tip of CNT was sharpened during the aging process. TEM image clearly indicates the removal of catalyst (Ni) metal during the treatment. The absence of Ni catalyst on the tip of the CNT after aging was confirmed from TEM analysis. It is believed that the Ni catalyst is removed by Joule heating during the aging.[3,4] The removal of metal catalyst during the aging are responsible for the enhancement (six times) of electron emission current.[5,6]

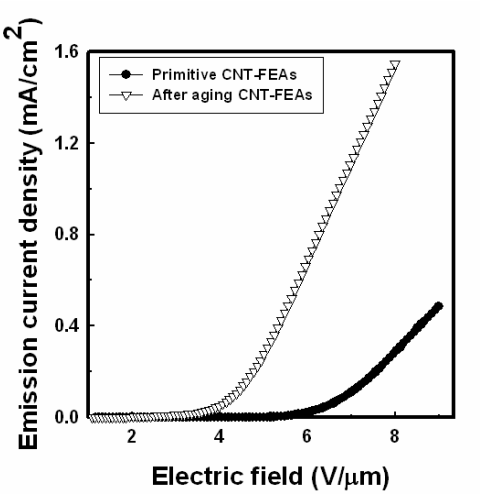


Fig 3. Electron emission characteristics of CNT – FEAs

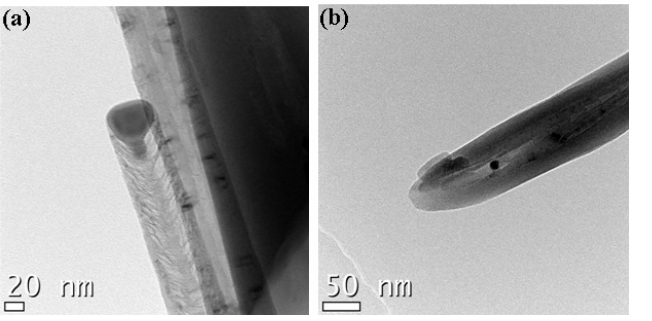
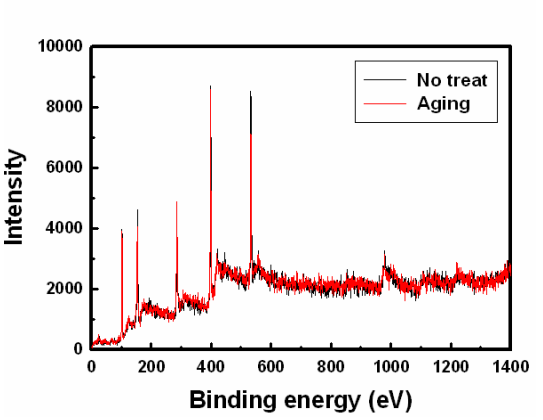


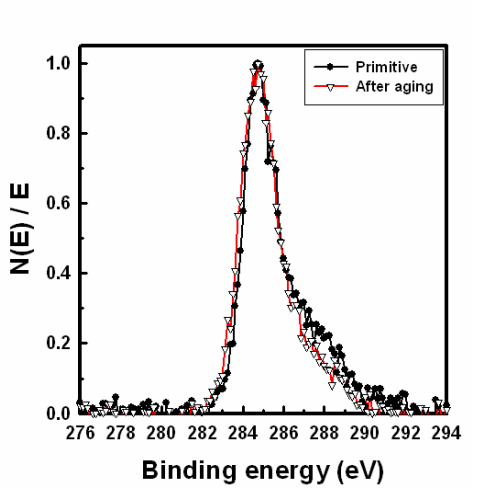
Fig 4. TEM images with aging treatment. (a) primitive (b) after aging of CNTs

Figure 5 depicts the XPS spectra of primitive and treated CNTs. The existence of peak at 284.75 eV in both the CNTs reveals the presence of amorphous carbon (C-H, C=H) arising from C_{1s}.[7] The measurement was performed without surface etching on CNT surface. As we can see in the TEM image, the graphite was surrounded by amorphous carbon.

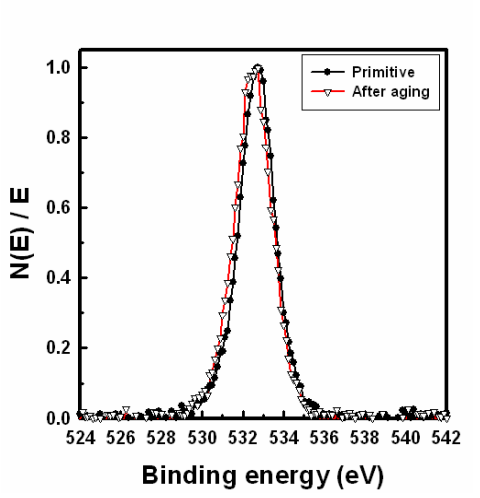
Moreover, it is noted that the pristine tube structure is not affected by the aging treatment. On the other hand, we observed a little bit shift in O_{1s} peak before and after aging process. The primitive CNT has only 532.7 ~ 532.8 eV for O-C was observed.[8] Thus, we strongly believe that the enhancement of emission property is due to the change of oxygen component rather than the change of carbon component during the aging treatment.



(a) Full range of XPS spectra



(b) C_{1s} spectra



(c) O_{1s} spectra

Fig 5. XPS spectra with aging treatment

An atomic concentration of carbon and oxygen atoms before and after aging treatment was calculated from Fig.5(c) spectrum. Table 1 shows the relative atomic ratio between carbon and oxygen. After the aging treatment, carbon concentration was increased. The increase of carbon ratio will be responsible to the emission current enhancement.

Table 1. Relative atomic concentration of C & O

	Primitive	After aging
C_{1s}/O_{1s}	1.092	1.925

Table 2. Relative atomic concentration of C & O after CNT surface etch.

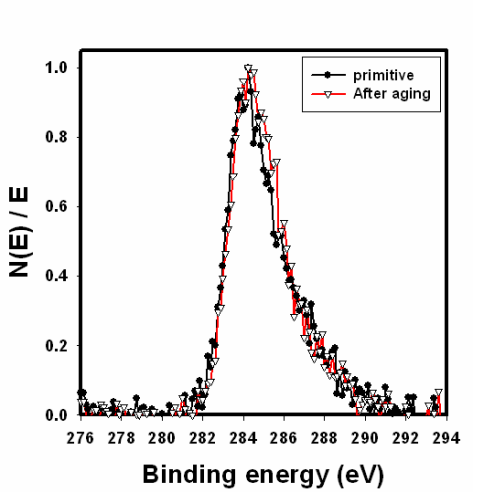
	Primitive	After aging
C_{1s}/O_{1s}	1.399	2.058

The CNT surfaces were etched using ion apparatus in the XPS system for depth profile analysis of the structural change of CNTs.

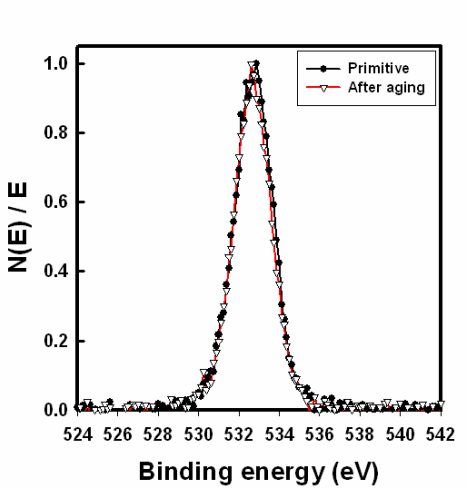
Figure 6 shows the measured XPS spectra after ion etch. From the XPS spectra, it is observed that both primitive and treated CNTs have c-graphite peak at 284.3 eV for C1s. This experiment confirms the hydrogenated amorphous carbon exist at the surface of CNT whereas C-graphite is present inside of CNT and so we expect a rather good characteristic if we remove the hydrogenated amorphous carbon present in the outer surface of CNT. From the XPS spectra, no difference was observed to O_{1s} peak for primitive CNT-FEA. Meantime, a difference was observed for the aging treated CNTs. The difference in 532.4 eV and 532.6 eV for O1s indicates the existence of O-H and O-C respectively after the aging. [9 - 11]

Table 2 shows the change of atomic concentration of carbon and oxygen atoms with aging treatment after ion etching. The ratio of atomic concentration of carbon and oxygen atoms increased after aging treatment.

From this study, the enhanced electron emission current was appeared to removal of oxygen atom. The removal of oxygen increase carbon concentration. Generally, the oxygen atom was known as degrading electron emission current. Thus electron emission the characteristic was improved due to the oxygen clearance.



(a) C_{1s} spectra



(b) O_{1s} spectra

Fig 6. XPS spectra of CNT after surface etch with Ar^+ ion

4. Summary

The effect of aging treatment on the electron emission properties of CNTs have been carried out. The emission property is increases about six times reason for the enhancement of emission is derived from the TEM and XPS analysis. The change in the structure and the removal of impurities after the aging treatment is responsible for the enhancement of emission property.

Above all, the aging treatment was very simple and effective process for post-growth treatment of CNT emitter. It will be applicable to electron emission source and can reduce the fabrication cost.

Acknowledgments

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