XPS Investigation and Field Emission Property of the Ar Plasma Processed Carbon Nanotube Films

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Carbon nanotube films were fabricated by the catalytic CVD method. Plasma processed time effects on the field emission property were studied. The atomic structure was observed by using X-ray photoelectron spectroscopy (XPS). The surface composition changes were observed on the plasma processed CNT films. The O1s/C1s signal ratio and the F1s/C1s signal ratio changed from 1.1 % to 24.65 % and from 0 % to 3.1 % with plasma process time, respectively. We could guess it from these results that the Ar plasma process could change the surface composition effectively. In the case of the original-CNT film, no carbon shift was observed. In the case of the Ar plasma processed CNT films, however the oxygen related carbon shifts were observed. This oxygen related carbon shift at higher binding energy implies the increment of amount of the oxygen. It's possible that the increment of these bonds between carbon and oxygen results in the improvement of field emission performance.

Keywords : XPS, Field Emission, Ar plasma, CNT

1. INTRODUCTION

After the recent discovery of the Carbon Nanotube (CNT)[1], many researchers have studied about the CNT due to its high aspect ratio, small curvature, good electrical conductivity, strong mechanical property, and chemical stability[2-5]. These CNT's remarkable features made it possible for CNT to apply to the wide range of researches. Especially, CNT has been considered as a superior candidate of the cathode in flat display panel and mechanical tip of AFM or STM[6,7].

Although some researches on the field emission properties of CNT were done[8,9], systematical studies on the field emission properties of the CNT related with the surface bonding state on CNT films caused by the attachment of functional groups through the plasma process have not been carried out.

Carbon nanotubes are composed of very strong covalent bonds, so that they are chemically stable. The field emission occurs at the cap of the CNT. Attachment of the functional groups to the cap of the CNT could control that field emission performance. Fortunately, the cutting of the chemical bonding starts from the pentagons on the cap.

In this paper, we investigate the surface change of the CNT films caused by the Ar plasma process. The effect of the surface change on the field emission properties was investigated. That surface change by the plasma process was analyzed by using the XPS spectroscopy. The relation between the surface change and the field emission property was discussed.

2. EXPERIMENT

2.1 Synthesis of CNT

CNT films studied in this paper were manufactured by the catalytic CVD method. They were grown at the gas

flow rate of Ar : NH_3 : C_2H_2 = 100 : 50 : 30 sccm at 700 °C for 20 mins on the sputtered Ni film. The sputtering power is 10 W and the sputtering process time is 1 hour, in order to control the Ni grain size. For the field emission measurement, the Ti layer was laid on the Si substrate firstly.

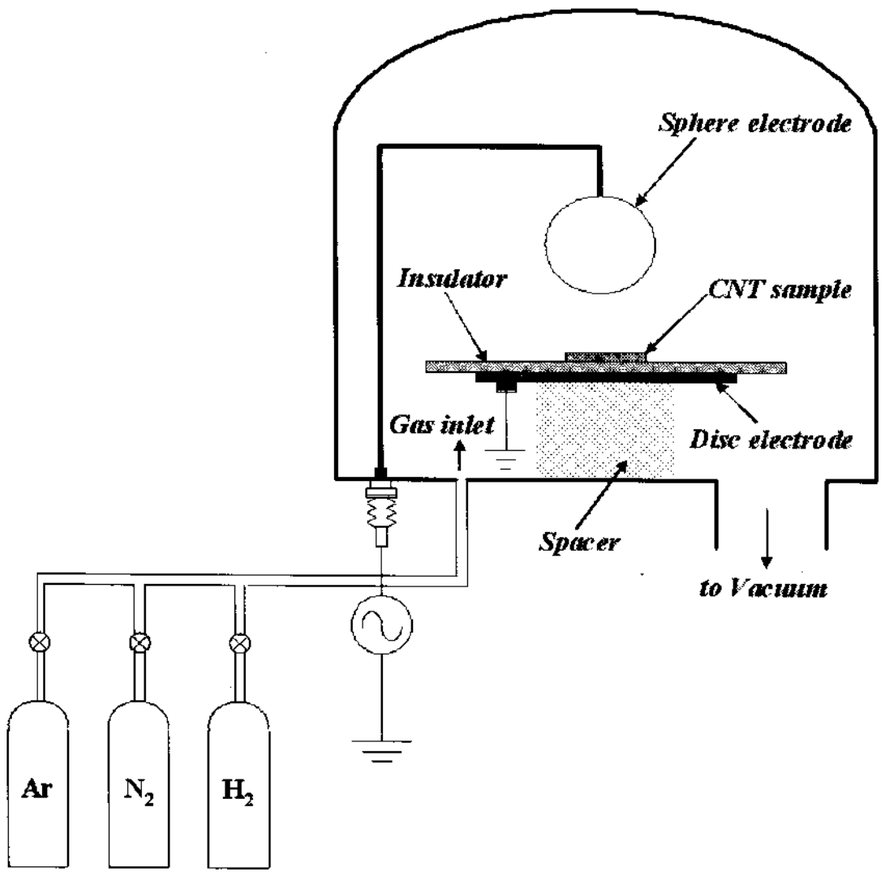


Fig. 1. Schematic diagram of the plasma process apparatus.

2.2 Ar plasma surface process of CNT

The CNT films were plasma processed in Ar, and the process time effects were examined. Fig. 1 shows the experimental set up of the plasma process. The plasma process chamber was evacuated to 10^{-2} Pa. Ar gas was introduced up to the degree of 20 Pa. At this vacuum level, the plasma process was carried out at the electric field of 2.4 kV/cm. AC voltage amplified through the neon transformer was supplied to generate plasma. The inter-electrodes distance was 2 cm. The Ar plasma process time was varied from 10 mins to 60 mins. After the plasma process, the CNT sample was stabilized for 1 h in the vacuum chamber.

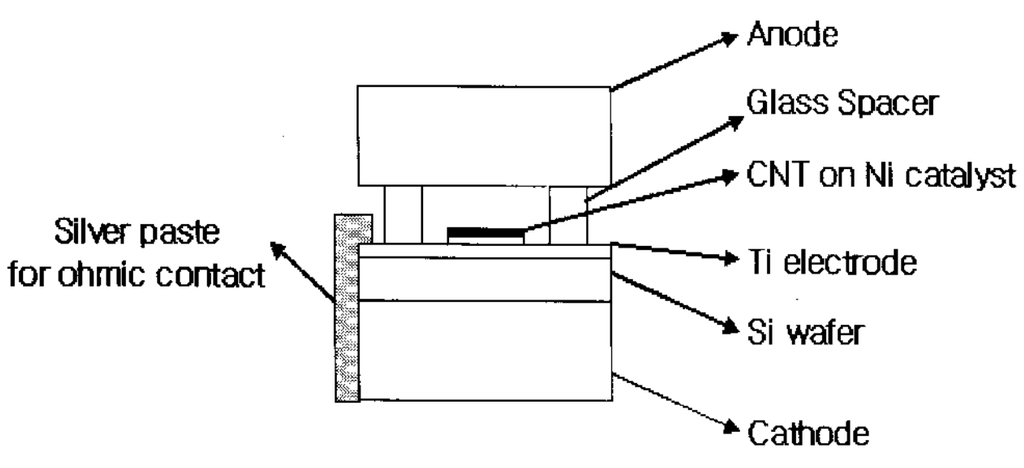


Fig. 2. Schematic diagram of the electrodes for field emission test.

2.3 XPS analysis

For investigation of the bonding state of the surface, X-ray photoelectron spectroscopy (XPS, JPS-9200, JEOL) was carried out by using the monochrome Al Kα X-ray.

2.4 Measurement of field emission property

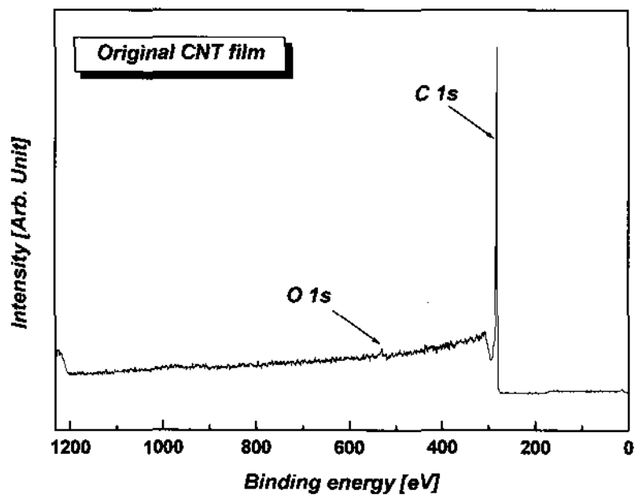
The field emissions properties of the CNT films were measured with digital multimeter (R6441C, Adventest) in an ultra high vacuum of ~10^{-6} Pa. The schematic diagram of the electrodes for field emission test used in this work was shown in Fig. 2.

3. RESULTS AND DISCUSSION

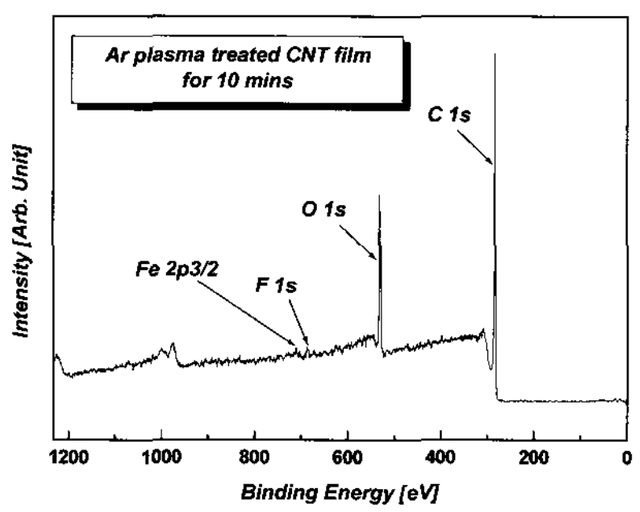
Figure 3 shows XPS wide scan spectra of the original CNT film and the plasma processed CNT films for 10, 30, and 60 mins. Very small oxygen peak can be observed for the as-grown CNT film, but the iron peak, the fluorine peak, and the oxygen peaks were observed for the Ar plasma processed CNT films. The iron might come from the stainless ball-type electrode used to generate the plasma plum. The fluorine peak should be injected from the Teflon sheet used as an insulating material. The origin of the oxygen peak is not so simple. There are two possible ways. One source is the water molecules in the air. Another is the water molecules attached at the wall of the vacuum chamber. In order to investigate these two possibilities, the ion bombardment process was done in the XPS inspection chamber.

In order to make clear the origin of oxygen peak, the CNT films were sputtered by an ion gun and were exposed to dry or wet air, respectively. The sputtering time was 400 seconds (40 secs × 10 times). That sputtering removes the attached functional groups to make the surface of CNT film active, so as to react with oxygen energetically during the exposing process. There are no significant differences between the CNT films exposed to wet or dry air (not shown in this paper). This means that the water molecules in the air don't play an important role to the attached oxygen on the CNT surface. Therefore we can conclude that the origin of the oxygen peak in the XPS spectra is the water molecules attached to the chamber wall from view of the results so far achieved.

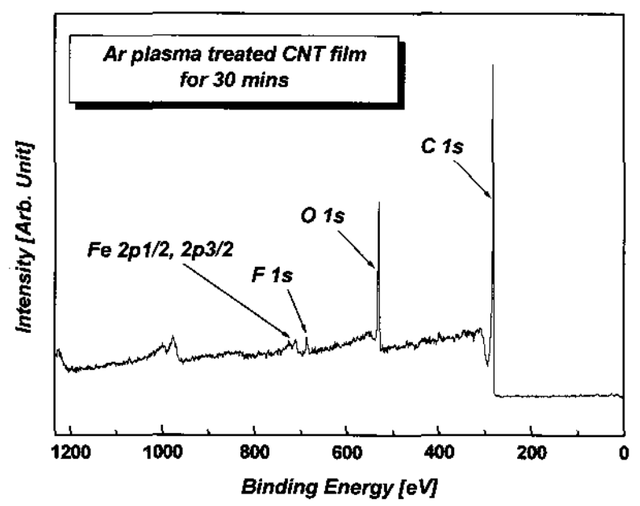
The O1s/C1s and the F1s/C1s signal ratios were obtained for the parameter of the process time as shown in Fig. 4. Each ratio was calculated from their peak heights. The O1s/C1s signal ratio and the F1s/C1s signal ratio changed from 1.1 % to 24.65 % and from 0 % to 3.1 % with plasma process time, respectively. We could guess it from these results that the Ar plasma process can change the surface composition effectively.



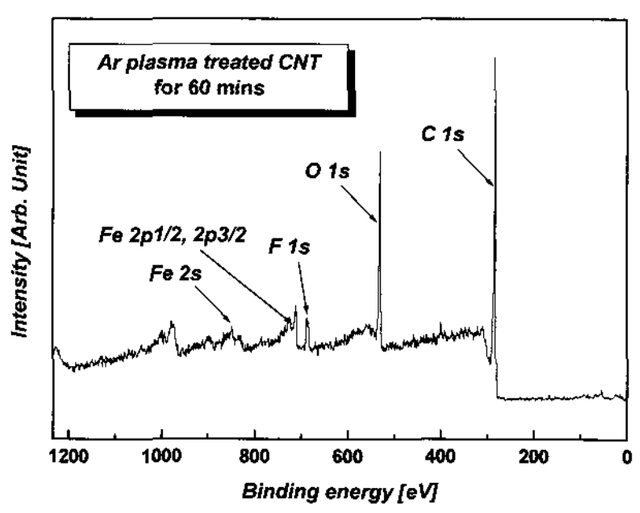
(a) Original CNT film



(b) Ar plasma processed CNT film for 10 mins



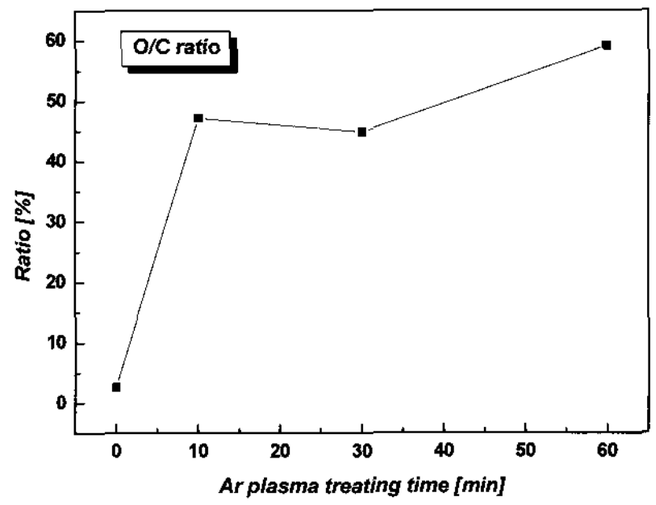
(c) Ar plasma processed CNT film for 30 mins



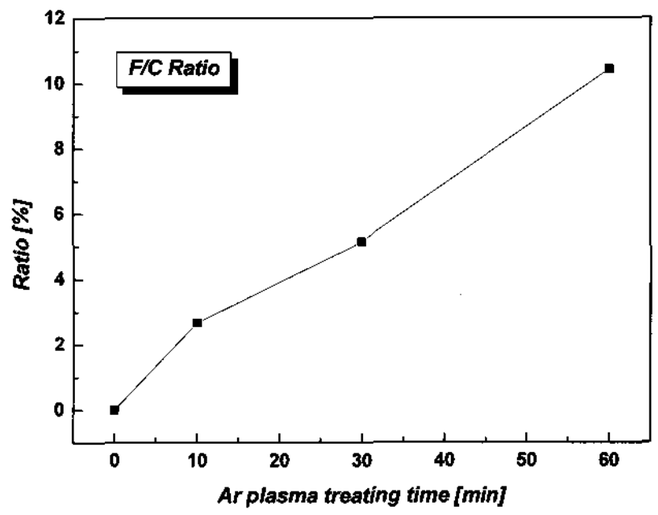
(d) Ar plasma processed CNT film for 60 mins

Fig. 3. XPS wide scan spectra of the CNT films.

The C1s narrow scan spectra of these CNT films give us the information about the bonding state between the carbon and other atoms. The C1s peak can be separated by sp^2 and sp^3 peak. The higher chemical shift of C1s can be observed.



(a) O1s/C1s ratio change



(b) F1s/C1s ratio change

Fig. 4. Surface composition ratios of the O1s/C1s and the F1s/C1s versus the Ar plasma process time.

The XPS narrow scan spectra of these CNT films were shown in Fig. 5. Every peak was curve fitted and divided into sp^2, sp^3, and another high chemical shift. For the original-CNT film, no carbon shift was observed. However for the Ar plasma processed CNT films, the oxygen related carbon shifts were observed.

When the bonding energy between carbon and oxygen is very strong, the chemical shift observed at high binding energy. The chemical shifts of the carbon were observed as 3.9, 3.1, and 3.7 eV for the Ar plasma processing time of 10, 30, and 60 minutes, respectively.

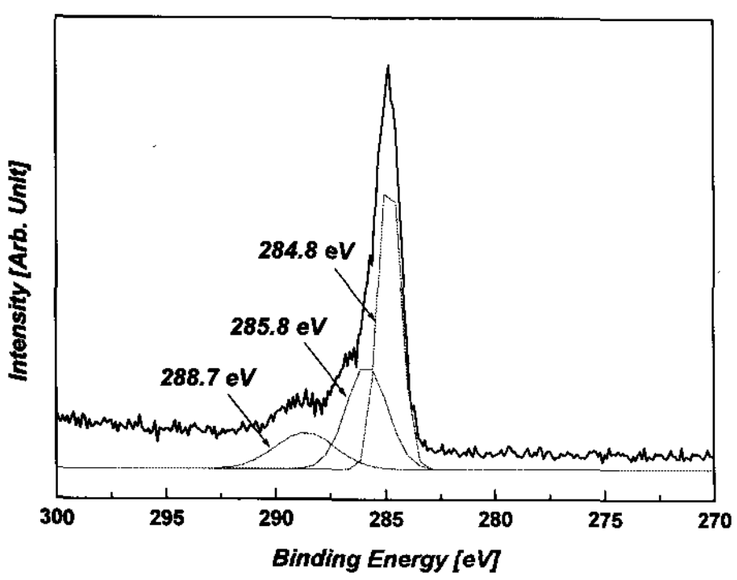
If the field emission current of CNT could be explained as F-N (Fowler-Nordheim) emission model, the current density should be[10]

$$J \propto \left(\frac{F^2}{\phi}\right)\exp\left(-6.8\times10^9\phi^{3/2}/F\right) \tag{1}$$

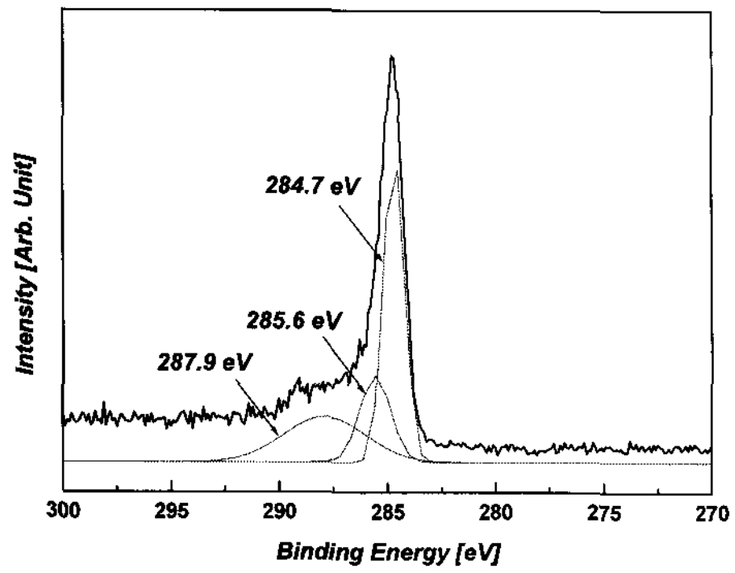
where, J, F, and ϕ represent the current density, the local electric field ($F = \beta E$), and the work function of CNT, respectively. The β is named as the field enhancement factor and usually defined by the aspect ratio of the cathode as shown in equation (2).

$$\beta = \frac{l}{d} \tag{2}$$

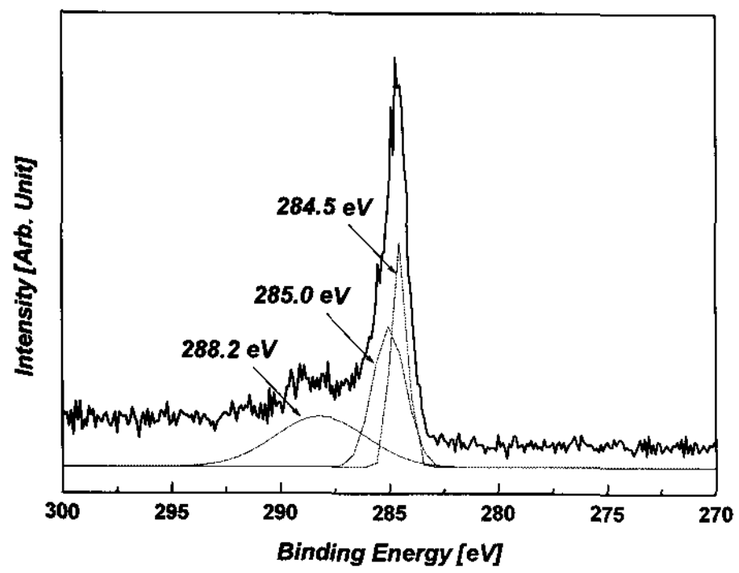
(a) Original CNT film



(b) Ar plasma processed CNT film for 10 mins



(c) Ar plasma processed CNT film for 30 mins



(d) Ar plasma processed CNT film for 60 mins

Fig. 5. XPS narrow scan spectra of the original CNT film and the Ar plasma processed CNT films.

where, l represents the length of CNT, and d is the diameter of CNT, respectively.

The field emission properties of the original CNT film and the Ar plasma processed CNT films were shown in Fig. 6. The field emission performance increased with increasing the Ar plasma processing time. In the case of the Ar plasma processed CNT films for 10 mins and 30 mins, slight performance improvements were observed. On the other hand in the case of the Ar plasma processed CNT film for 60 mins, outstanding improvement of field emission performance was observed. These results can be explained by using the surface composition ratio changes of the O1s/C1s as shown in Fig. 4. Y. Saito et al. reported that the field emission occurs at the pentagon site (need to form a curvature at the CNT cap) or the dangling bond of the CNT cap[11]. Ar plasma process can break the bonds between carbon and carbon, so as to create new bonds between carbon and oxygen. As the plasma process time increases, the amount of oxygen and carbon increased between carbon and oxygen increased. As the field emission occurs at pentagons or dangling bonds of the cap, increment of the bonds between carbon and oxygen means the improvement of the field emission performance.

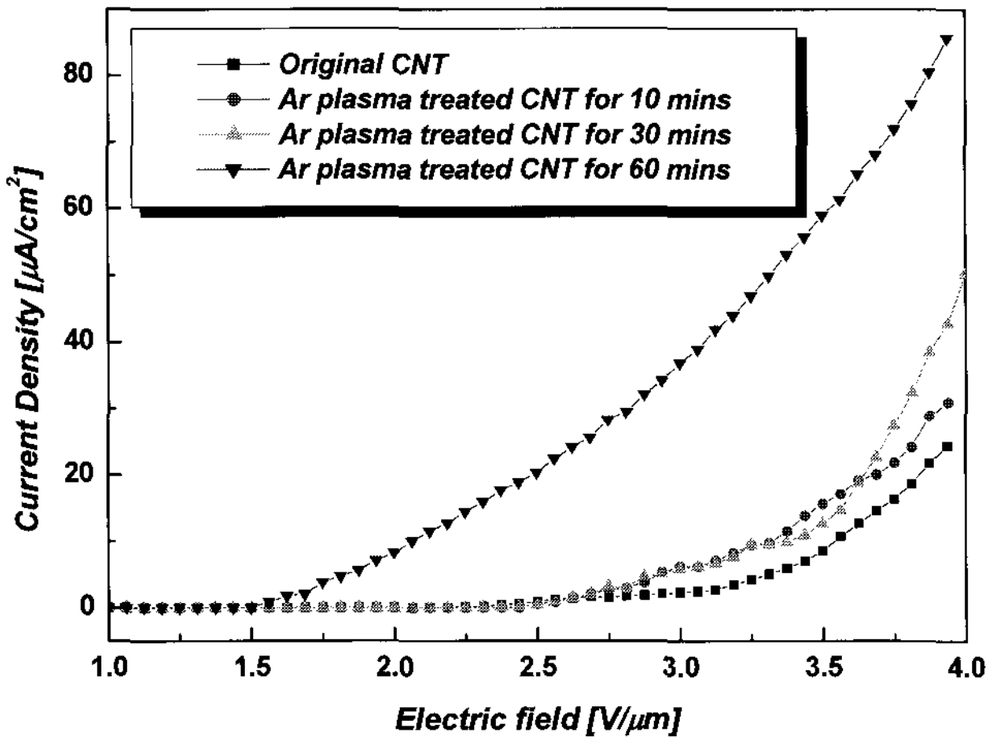


Fig. 6. Plot of field emission current vs. electric field for the original CNT film and the Ar plasma processed CNT films.

4. CONCLUSION

The surface change of the CNT films caused by the plasma process and its effect on the field emission property were investigated, and following results were obtained.

- The Ar plasma process could change the surface composition effectively.

- The amount of oxygen and carbon bond increased with the plasma process time.
- Because the field emission occurs at pentagons or dangling bonds of the CNT cap, the increment of the bonds between carbon and oxygen might play an important role in the field emission behavior. Therefore, increment of the bonds between carbon and oxygen leads to the increment of electron emission sites. As a result, the improvement of the field emission performance was achieved

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