Study on Carbon Nano Fiber Emitter for Field Emission Lamp

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Abstract

Properties of carbon nano fiber (CNF) as field emitters were described. Carbon nano fiber (CNF) of herringbone was prepared by thermal chemical vapor deposition(CVD). Field emitters mixed with organic binders, conductive materials and were prepared by screen-printing process. In order to increase field emissions, the surface treatment of rubbing & peel-off was applied to the printed CNF emitters on cathode electrode. The measurements of field emission properties were carried out by using a diode structure inline vacuum chamber. CNF of herringbone type showed good emission properties that a turn on field was as low as 2.1 V/μm and current density was as large as 0.15 mA/cm^2 of 4.2 V/μm with electric field. Through the results, we propose that CNFs are suitable for application of electron emitters in Field Emission Devices.

1. Introduction

Many researches associated with developing field emission applications are currently underway worldwide [1-2]. Most prototypes developed so far are based on Spindt-type microtips arrays, typically consist of Si or Mo [3-4] until 1990s. Despite the many advantages of Spindt-type, many researchers have been introduced the field emission source with nano-carbon materials having a strong potentials [5-6]. Carbon materials based on nano size are an allotrope of carbon that exists abundantly as natural and synthetic forms on earth. Their size are normally in the range from sub nano meters to several tens nano meters. There are, basically, 4 categories of nano phased carbon materials, such as carbon nano fiber (CNF), carbon nano tube (CNT), carbon nano cell (CNC, fullerene and related), and carbon nano particulate (CNP). They have similar atom structuresbut different shapes and sizes, so each has dissimilar in characters. It makes them vary in application also. C60, one of Fullerenes, has been consisted of 60 carbon atoms, 20 six membered carbon hexagonal planes and 12 pentagonal carbon planes and it's shape looks like soccer ball. CNThas been consisted of one or many number of graphene sheets and its shape is formed through rolling up to fibrous form with/without a joint and is classified into single and multi wall carbon nano-tubes. Due to their reliability, high efficiency and short switching time, CNT and CNF have been extensively studied using various methods in the application of nano display as cold emitter [5-7, 11]. These carbon nano materials can be realized by growing the nano carbon directly on a substrate pre-patterned with a catalyst, or by producing nano carbon materials-containing slurry or paste and subsequent patterning on a substrate [5-7]. Growing technology of CNT and CNF thin films are difficult to make a large size of cathode plate over large substrate area because of bad deposition uniformity. However, screen-printing technologies are well known as a low-cost process, and could be adopted to fabricate the large area of applied-vacuum field devices [10]. To optimize and improve several key technologies are necessary for the commercial base improving the surface morphology of nano-carbons, activating the surface to protrude and vertical alignment, and increasing the possibility of the quantum transport.

In this paper, we investigated the field emission characteristics of the various structured carbon nano fiber as a cold emitter using screen-printing technology. Various carbon nano fiber was synthesized by thermal CVD with diverse catalyst, reaction ambient and temperature. The microstructure of the CNF was investigated by high resolution field effect scanning electron microscope (FE-SEM), scanning tunneling microscope (STM) and transmission electron microscope (TEM). Also, the field emission properties of CNF emitters were checked by in-line vacuum chamber and prepared a fully vacuum packaged in a planar structure.

2. Experimental

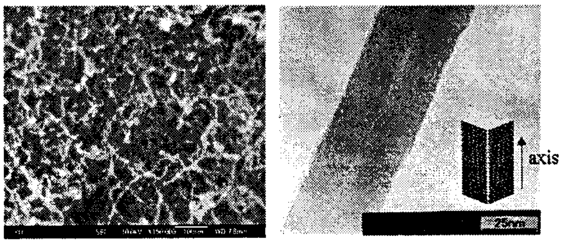
6.jpg Various carbon nano fiber of platelet, herringbone, tubular and accordion type grown by a thermal chemical vapor deposition (CVD) on each proper catalyst were used in the forms of the bundles without any purification process [9-11]. The CNF powders were mixed with polymer resin, organic vehicles, surfactants and conductive materials to be printable pastes. During preparing CNF pastes, appropriate organic vehicles and non-volatileorganic solvent were added to control viscosity in screen-printing process. In order to enhance the dispersion of CNF bundles intopastes, CNF pastes were well grounded together using mechanical turbulence and 3-roll mill. The mixed CNF pastes were screen-printed onto Ag/ITO coated soda-lime glass through the screen metal mask. In order to burn out the organic species, following the heat treatment of patterned CNF paste was done in the annealing furnace on air atmosphere. To activate the extraction electron from the edge of emitter, rubbing & peel-off method as a surface treatment was necessary to protrude efficient electron emissions from CNF surface.

For the anode plate, blending of three phosphors for green of ZnS:Cu,Al, blue of ZnS:Ag,Cl and red of Y_2O_3:Eu were also screen-printed with organic binders on the transparent ITO electrodes in the range of 12~14 ㎛ thickness. And then an additional firing process can get rid of extra organic vehicles.

Various type CNF emitters on cathode plate were characterized with diode structure of high voltage dc mode in ultra vacuum chamber. Additionally, the anode and cathode plates were then sealed with a thickness of 10mm pillar spacer in-between under inline high vacuum chamber. After the sealing process, non-evaporable getters in the panel were activated during the final heat-exchanging process. Finally, fully vacuum package of 9.5″ diagonal devices were prepared to show field emission image with planar structure.

3. Results

CNF of herringbone-type shows the microstructure of SEM and TEM in Fig. 1. CNF is consisted of many curved nano fiber in the range of 30-100nm unit size as prepared sample. The main characteristic of this nano fiber are their large hollow cores and thin wall, compared with the conventional tubular nano tube. Herring-bone type nano fibers in Fig. 1 have a small diameter, outer and inner ranging from 10-30 and 5-15 nm.



(a) SEM (b) TEM

Fig. 1. CNF structure of (a) SEM and (b) TEM image
그림 1. 헤링본-타입의 CNF (a) SEM 및 (b) TEM

Especially, the graphene layer stacking direction is resemble on the fishbone-like, and have many source of electron pumping site at each edge. Furthermore, herring-bone type CNF is a special kind of CNF with angles between the graphene plane direction and the axis of CNF in the range of 0-90 [7].

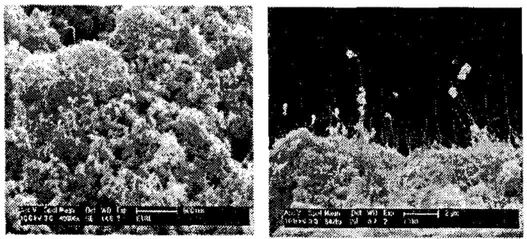

(a) (b)

Fig. 2. SEM image of (a) as screen-printed and after surface-treatment of herring-bone types CNF
그림 2. CNF 헤링본-구조의 표면처리 사진 (a) 표면처리 전 및 (b) 표면처리 후

Fig. 2 shows the surface morphology of herring-bone CNF paste before and after the surface treatment. After the screen-printing with herring-bone CNF pastes on the cathode substrate, emitter arrays on cathode glass plates were dried to evaporate the organic solvents. In Fig. 2 (a), it is clearly shown that the polymer binders wrapped around the herring-bone CNF surfaces, and had not seemed to disperse effectively. After following adjustable annealing treatment, some bundle of herring-bone CNF is activated partially from the adhesive surface of cathode plate. In order to activate the field emission sites, a proper surface treatment was adopted by a rubbing and peeling off method. This rubbing & peel-off method was gave rise to vertically align and to protrude herring-bone CNF emitters to the surface, as shown in Fig. 2 (b) [8].

Fig. 3 shows *I-V* characteristics of the electron emissions from diode type screen-printed herring-bone CNF emitters. The spacing of an anode-to-cathode was 250 ㎛ and measured directly in the vacuum chamber. The pattered cell size is 300 x 250 ㎛ and in a 3-inch diagonal panel with 96 x 64 pixels. In the case of as screen-printed sample, the emission current density of herring-bone CNF emitters was extremely low along with very poor uniformity. However, after the firing and surface treatment, the initial turn-on field was about 2.1 V/㎛. The emission current density was about 0.15 mA/cm^2 at a electric field of 4.2 V/㎛ with dc bias in vacuum chamber. The surface treatment of CNF pastes with polymer resin was essential to activate the emitter tips for screen-printing technology.

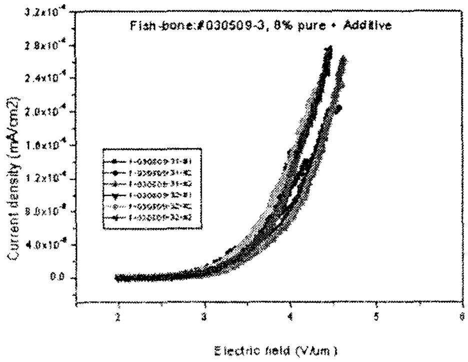
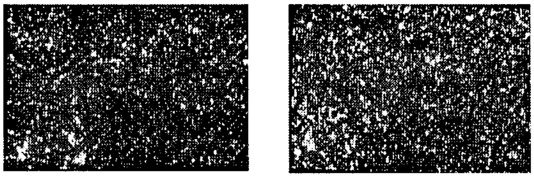


Fig. 3. I-V and Fowler-Nordheim plot of herringbone CNF in screen-printing process
그림 3. 인쇄방식으로 제조된 헤링본 구조 CNF의 전류 및 전압 변화

The field emission image of herring-bone type CNF is shown by using vacuum chamber of dc bias in Fig. 4. In the initial stage, the emission image was measured at an anode voltage of 1500V using green phosphor. The fluctuation and non-turn-on for every emitter did not necessarily coincide with current density from Fig. 3. Such a non-uniformity of emission image may be attributed to; different length of CNF from the surface; different poor alignment on the surface; non-uniform distribution; and non-uniform surface treatment. Even though the herringbone CNF emitter was applied to high anode voltage, resultant fluctuation of brightness and emission uniformity did not improved. This phenomenon need solve the effect why the CNF emitter of turn-on is different. At this time, the spacing of anode to cathode was 300m and applied voltage with a dc bias was constant at 1500 V.



(a) (b)

Fig. 4. The field emission image of (a) before and (b) after aging of herringbone CNF emitters
그림 4. 에이징 공정에 따른 발광이미지 변화 (a) 에이징 전 및 (b) 에이징 후

We packaged by using the in-line vacuum packaging process which anode, gate and cathode using two glass plate. Packaged and emission image of 9.5″ in diagonal is shown in Fig. 5. The fully vacuum-packaged panel was made with the help of pillar-type spacer of 10mm. In especial, we sealed the panel in an ultra high vacuum chamber, resulting in an ideal flat panel without an evacuation tube.

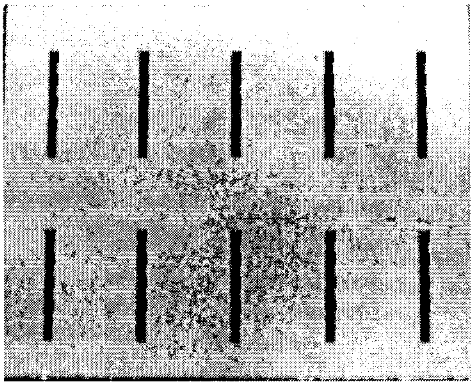


Fig. 5. The field emission image of herringbone CNF emitters with vacuum package in 9.5-inch planar type
그림 5. 진공패키징 된 9.5인치 플라나형 전계방출 이미지

After the sealing process, a laser or resistive heat activated the non-evaporable getter loaded inside the panel. The final vacuum of the packaged panel was approximately estimated in the range of 10-5 Torr. The measured brightness of showing text image was as high as 9000 cd/m^2 at an anode voltage of 8500 V. The stability and reliability of the panel was found to be strongly dependent on the vacuum level that was degraded by out-gassing from the cathode and/or anode during the panel operation. In order to suppress the out-gassing effect, a pre-processing was needed prior to the sealing [9].

4. Conclusions

We have measured the field emission characteristics of herringbone type carbon nano fibers. The screen-printing process was performed to fabricate a diode structure. Herring-bone type CNF emitter showed good emission properties before-and or after packaged panel. In addition, we proposed that the herring-bone CNF emitters will be one of the promising field emission lamps and application fileds in the near future.

References

[1] J.-M. Kim, W.-B. Choi, N.-S. Lee, J.-E. Jung, Diamond Relat. Mater. 9, p.1184 (2000).

[2] J.-L. Kwo, M.-Yokoyama, W.-C. Wang, F.-Y. Chuang, I.-N.Lin, Diamond Relat. Mater. 9, p.1270 (2000).

[3] W.-I. Milne, K.B.K. Teo, M. Chhowalla, P. Legagneux, G. Pirio and D. Pribat, Proceedings of the Society for Information Display 2002 International Symposium, p 1120 (2002).

[4] W.A. de Heer, A. Chatelain and D. Ugarte, Science, Vol. 270, p.1179 (1995)

[5] J.M. Lauerhaas, J.Y. Dai, A.A. Setlur, and R.P.H.Chang, J. Mater. Res. 12, p.1536 (1997)

[6] H.-J. Yang, S.-H. Yoon, Y. Korai, I. Mochidaand O. Katou, Carbon, Vol. 41, No. 3, p. 397 2003.

[7] K.-B. Kim, Y.-H. Song, C.-S. Hwang, C.-H. Chung, J.-H. Lee, I.-S. Choi and J.-H. Park, Proceedings of the 16th International Vacuum Microelectronics Conference, p.217 (2003).

[8] N.M. Rodriguez, A. Chambers, RTK. Baker, Catalytic engineering of carbon nano structure, Langmuir 11(10) p.3862 (1995)

[9] K.-B. Kim, H-G. Jung, S-G. Kim, S-H. Yoon, Proceedings of the Field Emission Workshops '04, (2004).