27.2: *Invited*: Carbon-Nanotube FED: Japanese National Project

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Abstract
The Japanese National Project "Carbon Nanotube FED" is developing a high image-quality and low power-consumption field emission display (FED) by applying carbon nanotube (CNT) to the electron source. A uniform electron source with a flat-film CNTs and fine structure triodes for suppressing the deviation of emission is required. For realizing an FED panel, it is also necessary to develop the glass-bulb technologies for vacuum sealing, and display technologies for driving the panel by circuit electronics and for evaluating the picture quality by measuring. By achieving these technologies, an FED compatible with conventional Cathode Ray Tubes (CRTs) will be realized.

1. Introduction

FEDs would be the most promising flat panel display device because of its following features[1]:

(1) Image Quality: Since the display principle is the same with CRTs, FEDs have just the same picture quality with CRTs. FEDs could present true-color and high-contrast natural pictures in wide dynamic range, quick motion pictures without blur with wide viewing-angle. A conceptual figure of high image-quality is shown in the following:

(2) Low Power: Since FEDs have high luminance efficiency (7 lumens per watt), they could operate with half the power consumption of other display devices.

(3) Small Investment: Since FEDs does not require expensive manufacturing facilities, the amount of investment would be small compared with other devices.

Among various field emitters[2]-[6], carbon nanotube is the most promising material for realizing large area electron source for FEDs[7]-[9], because CNT is a natural sharp pin enabling electron emission with low electric field. It is physically and chemically stable enough for bearing the damages by environments. Good quality CNTs are supplied with reasonable cost thanks to the preceding Japanese national projects on advanced carbon materials.

2. Implementation

This project is funded by the Ministry of Economics, Trade and Industry (METI) as one of the Nanotechnology Projects, and managed by the New Energy and Industrial Technology Development Organization(NEDO). It is entrusted to Fine-Ceramic Technology Research Association, Mitsubishi Electric Corp., Noritake Co. Ltd., Hitachi Displays Ltd., and Asahi Glass Co. Ltd., and partly entrusted to Osaka University, Osaka Prefecture University, Kyoto University, Nagoya University, and Mitsui Chemicals Inc.

3. Issues and Solutions

The issues of this project are (1) development of uniform electron source, and (2) development of panel technologies and evaluating the display quality technologies.

3.1 Uniform Electron Source

3.2

The most important problem for developing the CNT-FED is the deviation of pixel luminance caused by the deviation of emission properties among the cathodes. In order to solve this problem, this project concentrate on the development of flat CNT films, fine structure triodes, and activation technologies by surface treatment.

For developing uniform electron source by suppressing the deviations, increasing the number of emission sites is an effective solution. A fine structure triode is essential for increasing the emission sites.

The activation technology by CNT surface treatment is another key issue of developing the CNT electron source. This project is making research on the laser irradiation method.

3.2 Panel and Evaluating the Display Quality Technologies

The other issues for developing the FED are panel technologies for vacuum bulb. This project focuses on the development of low cost glass bulb without spacers and low temperature sealing techniques.

A novel glass structure of the bulb is investigated for coping with the atmospheric pressure loaded on the front and rear glass panels when they are evacuated without spacer.

A new sealing process below 400 degrees for avoiding the thermal stress caused by the conventional 450 degrees sealing process is studied.

4. Latest Achievements

The followings are the latest achievements reported in the Annual report for the 2004 fiscal year[10].

4.1 Uniform Emitters by Thermal CVD

A uniform fine-pitch cathode was investigated for TV application by thermal-chemical vapor deposition, which was deposited on fine metal-lines-frame with carbon nanotubes of about 40nm in diameter. The surface flatness was measured to confirm the required performance, so that a 200µm-pitch cathode was manufactured to research the practical structure for TV device.

The ideal CNT-layer-surface-morphology was investigated by laser irradiation. As a result, the emission was greatly enhanced at appropriate laser-energy-density. It indicated that the uniform surface potential and the number of CNT tips were important for enhancing the emission.

For lower driving voltage, smaller diameter was requir ed for CNT. An experimental approach was performed by increasi ng the substrate temperature. As a result, a smaller diameter of 10-15nm was deposited on fine metal electrodes.[11]

4.1.1 Elucidation of Growth Mechanism of CNT

1) Analysis of growth mechanism of CNTs

Growth process of CNTs in thermal CVD method was investigated by varying growth time. It was found that protrusions or small particles containing catalytic metal was formed at the initial stage of growth and then CNTs began to grow from them. CNTs after the growth held catalytic particles at both ends (i.e., at the tip and the base).

2) Simulation of electric field over a CNT layer

Electric field strength at the tips of CNTs existing in a CNT layer with a networked structure was calculated. When the CNT film forms the web-like structure, variation of the field strength at the CNT tips due to the height difference is reduced (i.e., uniformity of field is increases) compared with the vertically-aligned CNTs.

4.1.2. Synthesis and Growth Mechanism of DWNT

Synthesis and characterization of double wall carbon nanotubes for filed emission display have been studied in terms of catalyst-supported chemical vapor deposition (CCVD) using high-temperature resistant zeolite materials. We think that the following three results are crucial to the further high yield synthesis of DWNTs: (1) High-temperature resistant zeolite materials are mandatory for the efficient generation of DWNT. Acetylene and ethylalcohol are the best reactants when titanosilicates and boronsilicates are employed, respectively, for the DWNT synthesis; (2) The optimum growth temperature at the DWNT synthesis for the both zeolites is 900℃; (3) Thick (4-5 nm in diameter) and thin (2.5-3 nm) DWNT have been selectively synthesized when titanosilicates and boronsilicates are used, respectively, as support materials.

4.2 Development of uniform printed CNT emitters

We have developed uniform printed CNT emitters. First, we searched for CNT materials as field emitters. As a result, we found that a kind of multi-wall CNT material grown by CVD method gave an excellent field emission characteristics. The CNT material whose averaged diameter is less than 10 nm shows 10 mA/cm2 emission current under the electric field of only 1.3 V/µm. The CNT material contains some particles with the diameter of several µm and it prevents perfect dispersion of the CNT material in the paste. This problem can be solved by our tailored dispersion method. We printed the well dispersed CNT paste on a glass substrate and confirmed that the flatness of printed CNT film might be within the deviation of ±3µm. The printed CNT film gave the excellent emission characteristics. The high emission current density of 75mA/cm2 is obtained at the low electric field of only 3V/µm. This excellent field emission characteristic is due to the reduction of mechanical damages during the fabrication process of the paste.

4.3 Development of Surface-Treatment

A surface-treatment method by laser irradiation has been proved effective to enhance the emission ability of CNTs. Emission ability dependence on laser sources, wavelength, irradiation patterns and laser energy has been investigated. By optimizing the conditions, the turn-on electric field of 2 V/µm and the emission current density of 4mA/cm2 at the electric field of 5 V/µm were achieved. The irradiation level was low enough not to damage the triode electrodes.

Figure 1 illustrates the effect of activating the CNT surface by laser.[12]

4.3.1 R&D of Surface treatment technology

1) Development of UV laser surface treatment for printed and CVD CNT cathodes

A UV laser source for a stripe beam system has been introduced to improve the emission behavior of CNT cathodes. Dependence of UV laser wavelength, power density, and irradiation atmosphere on improvement of CNT cathode characteristics has been investigated for surface treatment of CNT cathodes.

A homogeneous distribution of emission site with three orders of magnitude higher emission current density has been obtained by laser irradiation with wavelengths of 248 ~ 349 nm. An appropriate power density at and above 4MW/cm2 was found to result in the turn-on field of less than 1V/um. Laser irradiation in oxygen ambient was found to be most effective in improvement of emission behavior. The characteristics of CVD cathodes have been investigated and it was confirmed that the surface of the cathodes should further be treated for the improvement.[13]-[15]

2) Development of low energy ion surface treatment from plasma for printed CNT cathode

Low energy Ar ion beam from plasma has been irradiated to printed CNT cathodes to improve electron emission behavior.

Plasma treatment of CNT cathodes with a plasma power of 60 W for 3 ~ 5 min was found to increase the number of electron emission site.

4.3.2 Investigation of physical phenomena in improvement of electron emission properties of CNT by surface treatment

Electron emission properties of the carbon nanotubes with and without laser irradiation, were measured in ultrahigh vacuum with a needle collector. The electron emission from the sample that had been irradiated by high power lasers showed the property significantly different from the other samples, having a lower threshold voltage. The difference was analyzed by the S-K chart. The electron emission property of the high-power laser-irradiated sample located at upper right in the S-K chart, which means the cathode has a lower work function or higher voltage-field conversion factor.

The difference could not be explained in terms with the change in work function, and thus it implies that structural change is major reason for the improvement. Besides these results, detailed measurements were performed in order to ensure the obtained results and their interpretation.

4.4 Process Development of Fine-Structure Emitter

A process for fabricating a number of micro-gate holes on CNTs has been developed. A new material, silicone-ladder polymer., PPSQ(Polyphenylsilsesquioxane) was used for insulating the cathodes from gate films. PPSQ has excellent properties of simple deposition process, thermo-stability, high breakdown voltage and low out gassing rate. PPSQ enabled to fabricate high aspect-ratio micro-gate holes to guarantee the electric-field uniformity on the CNT emitters and improved the luminance uniformity.

The dry and spin-wet etching method was developed to obtain well-controlled micro-hole configuration using PPSQ. The treatment condition has been optimized to satisfy the etching property. The micro-gate holes were successfully fabricated without damaging the CNT on the bottom of holes.[16] Figure 2 shows an example of fabricating fine triodes using PPSQ.[17]

4.4.1 Low-temperature growth of vertically aligned carbon nanotubes in tiny holes

In order to fabricate vertically-aligned high-quality carbon nanotubes (CNT) at a low-temperature (below 550℃) CVD process, 1) preheating of the reaction gas, 2) carbonization of the catalysts and 3) selection of the binary catalysts, have been investigated and the following results have been obtained. Figure 3 shows an SEM image of Micro emission site fabricated by low-temperature CVD.[18]

1) Preheating of the Reaction Gas

The preheating at 700C enhances the reactivity of a carbon source gas of acetylene and contributed to the decomposition of the gas i n high efficiency on the surfaces of the catalysts heated at 550℃.

2) Carbonization of the Catalysts

The catalyst of iron is activated by the carbonization using a mixtu re of a carbon source gas and an inert gas at a temperature below 5 00℃.

3) Selection of the Binary Catalysts

For the selection of binary catalysts, we have examined Al/Fe, Fe/ Ti and Co/Ti. It has been confirmed that using Al, which has a low melting point, as a grounding film facilitates Fe-particle formation at low temperature and also prevents the Fe part icles from aggregation. Fe/Ti and Co/Ti catalysts, which have diff erent limitations of atom ration for Ti in solid solutions of Fe and Co provided different results. The performance of Fe catalyst is de graded in Fe/Ti. This might be caused by the fact that Ti is easier t o intermingle with Fe.

On the other hand, Co/Ti animates Co catalyst to grow aligned CNTs at a low temperature even without the carbonization process. This is because Ti is difficult to intermingle with Co. It is evidenced that the three kinds of techniques are very effective in the CNT growth at a low temperature of 550℃. For the investigation of the field emission properties, the measurement system, which can be performed for a single CNT, has been prepared and its pilot study has been made.

4.5 Development of Display Fabrication and Quality Evaluation Technology

The measurement system of current-versus-voltage characteristics of individual pixel was developed. The system has a current-level resolution of $\pm 0.005\,\mu A$ with the accuracy of $\pm 0.01\,\mu A$. The system scans every pixel of a FED panel and the current data are translated by an 11 bits of AD converter ($\pm 0.005\,\mu A$ resolution is guaranteed) and realizes the accuracy of $\pm 0.01\,\mu A$. The current distribution of FED can also be measured with this system.

An evaluation system of image quality was developed by using a CCD camera. This system has a resolution of 1% of the peak luminosity and has a chromaticity resolution of ±0.001 degree. The diameter of the beam spot on the anode can also be measured with the accuracy of 0.1mm or less by combining a CCD camera and a zooming lens. Using this system, the electron beam was observed to focus less than 100μm.

4.5.1 Development of panel structure for CNT-FED

The main subject in this research is to develop a basic panel structure without spacer applicable for a large size screen and manufacturing technologies for the components in order to realize a high quality and low cost FED.

Using a numerical structure analysis, it has been investigated to reduce tensile stresses induced by vacuum on the glass panel that are extremely high compared to the fracture strength of the glass or the sealing material. As a result, we have invented a new panel structure composed of a glass envelope for hermetic sealing and metal components for pressure proof. In particular, a considerable reduction of the tensile stresses at the sealing portion could be attained. In addition, it has been studied to introduce pre-compression on the glass surface by thermal tempering or chemical tempering which can allow a considerably high tension at the screen edge to be borne before the tensile strength is exceeded. So, we have made a decision of elaborating a new spacer-less panel structure with a high reliability.

Moreover, we have performed several preliminary tests including press forming of a front glass panel with a high strain point and a shallow box-like shape. As a result, it has been understood that some issues have been originated from its high working range and the unique shape of the front glass. Furthermore, it has also been investigated to elaborate thermal tempering and chemical tempering methods suitable for the front glass panel.

4.5.2 Development of sealing technology at a low temperature

The main issue in this sub-theme is to develop a lead free and heat-resisting sealing material, which can be used at a low temperature under nitrogen atmosphere, in order to avoid thermal damage of the CNT emitters and electrode structure stacked in multi-layers.

In investigating several heat-resting organic materials, polyimide polymer was selected as a basic adhesive. The mainframe structure of the polyimide has been designed so that it could show a highly adhesive property and a high heat-resistance. Furthermore, higher fracture strength at a high temperature compared to that of a conventional thermoplastic-polyimide was obtained, introducing a thermosetting polyimide structure.

Moreover, synthesizing a composite material has been pursed preliminarily in order to satisfy enough required characteristics as a sealing material for CNT-FED. It was found out that a kind of surface treatment was most effective for stabilizing dispersion of fillers to the polyimide resin and found out that anisotropic fillers could effectively lower the coefficient of the thermal expansion.

4. Acknowledgements

5.

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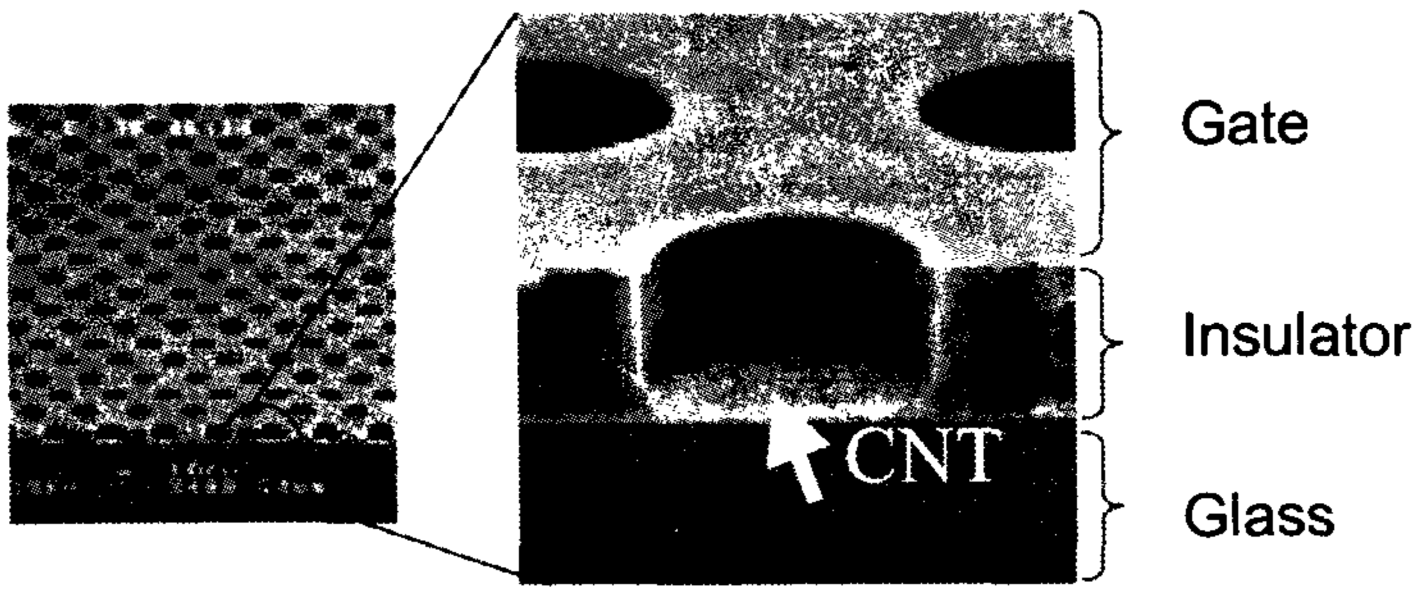

Figure 1. SEM Images of CNT Triode Fabricated by Printing and Etching

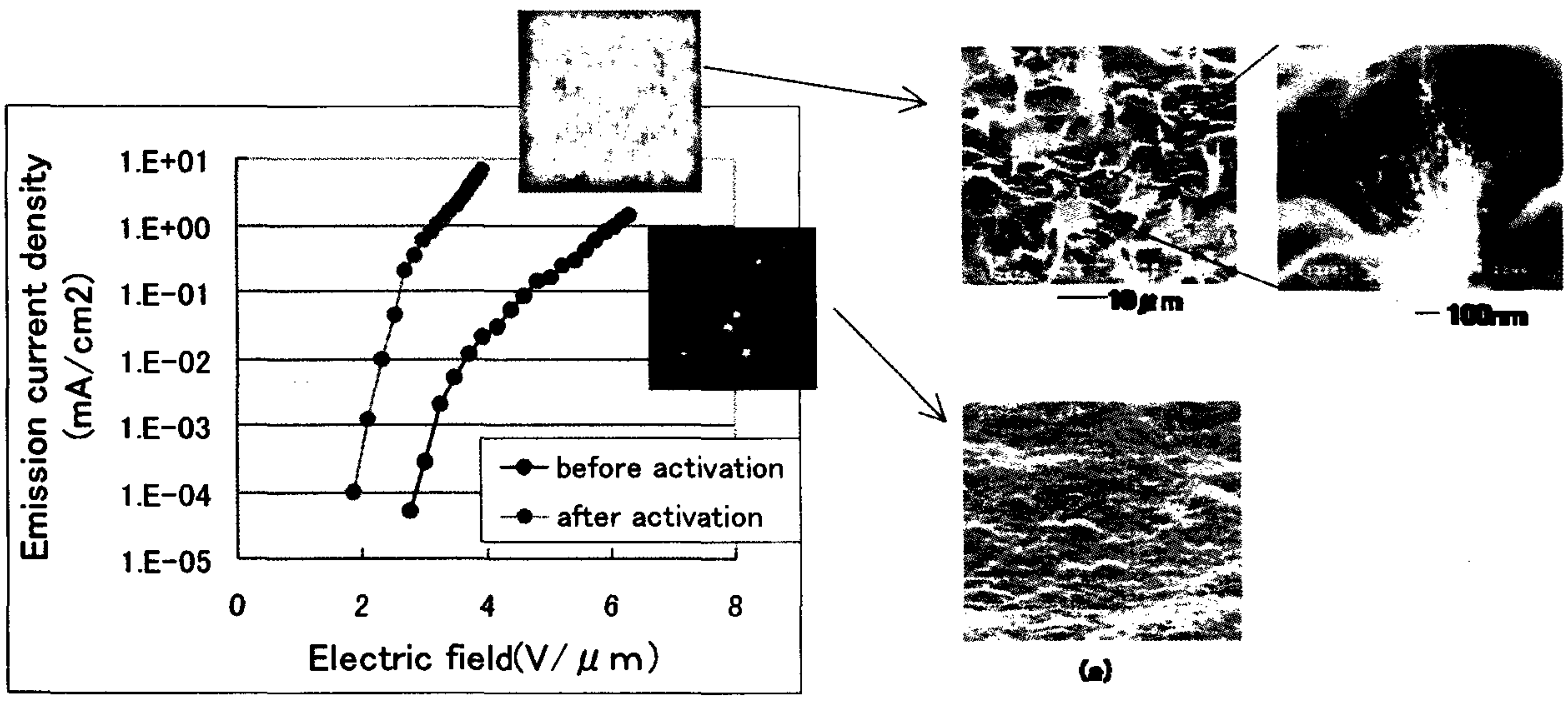

Figure 2. Effect of CNT Activation by Laser