Unique carbon-nano-structure for high quality electron-emitter to be employed in a variety of applications

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There have been many trials to employ nano-carbon materials, such as carbon-nano-tubes and nano-diamond films, as electron-emitter. Several reasons exist why the nano-carbon materials are good for the emitter. They are, in addition to (a) unique morphological shapes of the materials good for the emitter– the high aspect ratio of the carbon-nano-tube is a good example–, (b) sturdiness(they can even be formed in a plasma), (c) high thermal conductivity (current density in the electron-emitting-nano-structure is high, thus it is vital to provide effective Joule-heat dissipation), and (d) easiness of the fabrication of the electron-emitting carbon materials. In order to fabricate good electron emitters, we have long been trying to employ a variety of fabrication CVD methods and fabricating conditions (starting CVD gas, pressure, temperature, substrate materials and so on).Then recently our emitters have shown a world-top-ranking property: very low turn-on-voltage(0.5V/μm induce 10μA/cm^2 of emission current) and high current at low applied voltage with gap distance of 1mm(1mA/cm^2 at 1.1V/μm and 100/ at 2V/μm). This excellent property comes from a carbon-nano-structure which we call CNX(Carbon-Nano-eXit). In addition, these emitter can be formed on a variety of substrates(Ni, Ni-Cr, SUS or others), in forms of wire or pipe, very quickly. Namely, by one reactor, it is possible to fabricate 50$\sim$100 km of "wire or pipe type emitter" per month.The wire type emitter is good for both high field concentration and avoiding the so-called "edge-effect".Then using these emitters, we are able to fabricate Mercury-free fluorescence lamps with high efficiency ($\sim$60lm/watt) and high brightness of more than 10^5cd/m^2(white-light).

Keywords: Electron emitters; CVD diamond; carbon-nanostructure; carbon nano wires.

Se han llevado a cabo varios intentos para construir emisores de electrones a partir de materiales nanoestructurados a base de carbono en la forma de nanotubos y películas de nanodiamantes. Existen varias razones para considerar a estos materiales como emisores de electrones. Estos poseen: (a) especiales aspectos morfológicos adecuados para buenos emisores, (b) durabilidad (se pueden forma a partir de plasma), (c) alta conductividad térmica, (d) fácil fabricación. Con el objeto de fabricar buenos emisores de electrones, hemos utilizado una gran variedad de métodos de CVD y diferentes condiciones de fabricación (gas precursor inicial, presión, temperatura, diferentes substratos, etc.). Recientemente, nuestros emisores exhibieron propiedades excepcionales a nivel mundial: voltaje de encendido muy bajo y alta corriente con bajo voltaje aplicado (0.5V/μm para inducir 10μA/cm^2 de corriente inducida) y distancia de brecha de 1 mm (1mA/cm^2, 1.1V/μm y 100/, 2V/μm). Estas excelentes propiedades se deben a la forma de carbono nanoestructurado llamado CNX(Carbon-Nano-eXit). Además, los emisores pueden depositarse fácilmente en una gran variedad de substratos (Ni, Ni-Cr, SUS, entre otros) en la forma de hilos o tubos. Por ejemplo, un reactor puede fabricar en un mes entre 50 a 100 km de emisores en la forma de hilo o tubos. Los emisores de hilo son adecuados para campos altamente concentrados y evitan los "efectos de bordes". La utilización de estos emisores permite la fabricación de lámparas fluorescentes sin mercurio de alta eficiencia (aprox. 60 lm/Watt) y brillo superior a 10^5 cd/m^2 (Luz blanca).

Descriptores: Emisores de electrones; carbono nanoestructurado; diamante CVD.

PACS: 61.46.+w; 79.70.+q; 81.05.Uw; 81.07.-b; 85.45.Fd

1. Introduction

Many reports have been published on electron emission from nano-structured carbon films including CVD diamond thin films and carbon nano-tubes. The main motivation for such studies is application of the electron emitters for flat panel display(FPD) to replace CRT display (or television), which has the disadvantages of being too thick and heavy. Because, the application may contribute the solution to these problems through the possibility of manufacturing of thin and lightweight displays due to following reasons. As shown in Fig.1, the cause the thick CRT screens is that only one electrons (a hot cathode is widely used) are electrically accelerated and magnetically scanned over a phosphor that emits light creating the image. However, the use of N electron guns(cold cathode would be preferable) could enable a thickness reduction to L/N as illustrated in the figure. Thus an array of electron guns located on a planar surface would enable ultrathin and lightweight displays or pixels. At the same time, it is expected that the emitter can be applied to manufacture high brightness light sources. Indeed, the emitted light intensity of $\sim$100,000 m^{-2} has been attained by employing carbon emitters(such as carbon nanotubes [1,2] and diamond [3]). The value for commercially available fluorescent tubes is $\sim$3,000m^{-2}. As described in the abstract of this paper, we have been trying to fabricate good emitter through fabrications of carbon-nano-materials. So starting from basics of the emission, we will explain how the carbon –nano-materials have been employed and developed for the better

quality. And finally, how the exellent emitter from the new material named as CNX(Carbon-Nano-eXit) was found and fabricated.

2. Factors to Control Electron Emission from Diamond and Carbon Materials

2.1. (Carbon Nanotubes and others)

The degree of electron emission observed in a variety of carbon materials (CVD-diamond thin films, carbon nanotubes, nanowalls and others) is thought to be governed by the existence of graphite components of high electrical conductivity within the materials.

For example, the emission current of polycrystalline CVD-diamond thin films is inversely proportional to the grain size and it has been concluded to originate from the existence of graphite layers at the grain boundaries. Thus selection of deposition conditions that increase the graphite content within the CVD-diamond (that is, conditions that would not be favorable for the growth of high quality diamond films) yield films with electron emissive ability.

Thus, as schematically shown in Fig. 2, diamond films with good electron emission properties are composed of high resistivity diamond grains with gaps or grain boundaries filled with high conductivity graphite rods or layers: referred to as "nano-graphite chips".

The electron emitting diamond films can be employed for light emitting devices. For example, a simple two-electrode or diode device is formed by providing an electrode (cathode)

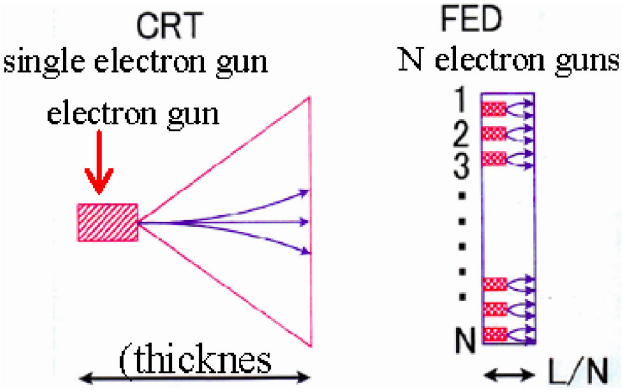

FIGURE 1. Principle of making display thickness thin with increasing number of electron guns.

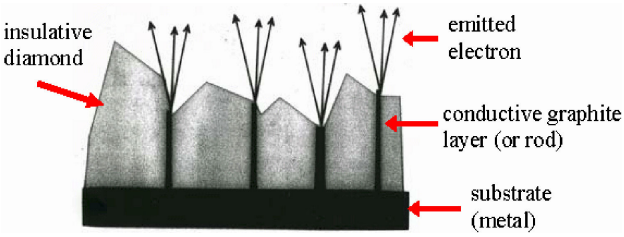

FIGURE 2. Model for diamond thin film electron emission.

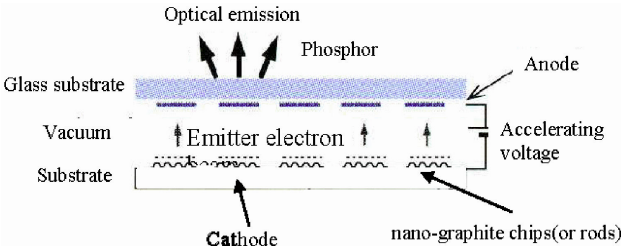

FIGURE 3. Structure of field-emission display (diode or two-electrode type).

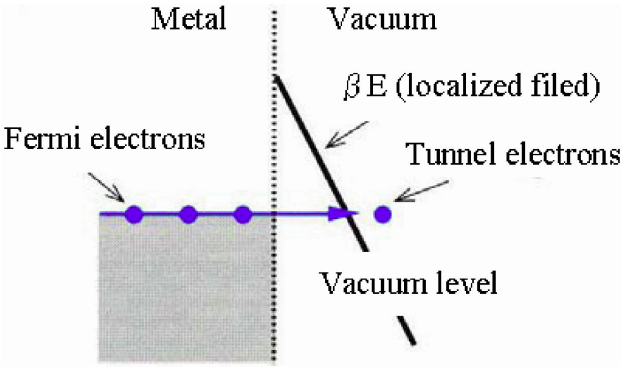

FIGURE 4. Electron (or electric field) emission phenomena madel (tunneling is easier at sharper slope for large β.)

below the diamond film and an anode is located at a small distance from the surface of the low quality(or electron emissive) diamond film containing the nano-graphite chips, as schematically illustrated by Fig.3. And also three-electrode or triode type device can be manufactured.

Application of an electric field between the (cold) cathode and anode induces the emission of electrons and they hit phosphor on the anode to emitt light. Thus, if the nano-graphite chip is thought of as a small raised section on the metal electrode, then, as shown in Fig. 4, the vacuum level is inclined when an electric field is applied and electron are emitted from the protruding area, at which the field is concentrated to give rise to a strong electric field, due to a tunneling process similar to field emission from metals. The local concentrated electric field (Eloc) at the ultrafine protrusion depends on its shape and can be much larger (β-times) than the applied field, E, and is expressed as, Eloc=βE. Needless to say, the larger the factor β, the easier it becomes for electron emission. If the protrusion is considered as an electrically conducting chip with a length, ℓ and radius, r, then the factor $\beta \sim \ell$/r. From this relationship it can be seen that carbon nanotubes, which have high electrical conductivity and aspect ratios, should exhibit excellent electron emission characteristics. The electrons are injected(or emitted) from Fermi-level of the metallic or conductive graphite into vacum out of the graphite-surface area or cathode area through tunneling and then these injected electrons are accelerated by the external electric field at the surface towards anode area. Then usualy,

the current density due to these electrons can be discribed by the Fowler-Nordheim equation:

$$J_{F-N} = aE^2 \exp(-b\varphi^{3/2}/\beta E) \quad (1)$$

Here E is the average applied electric field and φ the height of the potential barrier and a, b are constants.

But, when the injected electron density is large enough, the current density may be analyzed by a sense of the space chrge limited current[4]. So, the expression of the emission current may deviate from J_{F-N} or (1).

However, since we are interested in fabricating good emitters, we can forget rather possibly complicated (as expected) but more academic expression of the current density(J), like one discussed already [4], and replace it by the practrical or phenomologically straight forward expression Jpheno or (2):

$$Jpheno \propto NC_{rod}E_{loc} \quad (2)$$

where, N is the density of protrusions ("rods), E_{loc}(=βE) is the local electric field and C_{rod} is the conductance of one rod.

It can be seen from (2) that the following conditions (a)-(c) must be satisfied in order to achieve high current densities: (a) high density of rods, N, (b) highly conducting rods (of course, the rods themselves should exhibit very low or no contact resistance to the substrate) , and, (c) strong localized electric field. However, the current density can decrease if the density of rods is too large due to so called "screening effects" suggested by Nilsson *et al.* [5] to be described later in the next section : "Design Considerations for Fabrication of Carbon Nano-materials for Good Emitters".

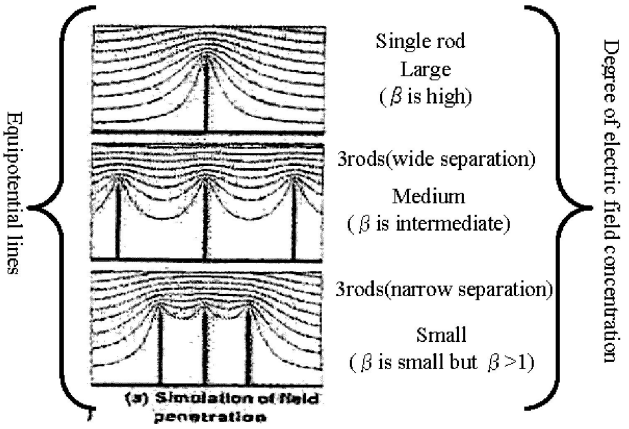

FIGURE 5. Simulated variation of equipotential distribution with number and separation of the same metal (or highly conductive) rods. Degree of electric field concentration (β) an localization of electric field decreases (Large, Medium, Small) with increasing number of rods.

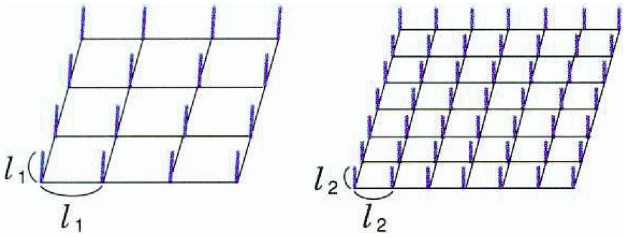

FIGURE 6. Differences in emission sites of CNT rods with ideal separation buy different length ($l_1 > l_2$).

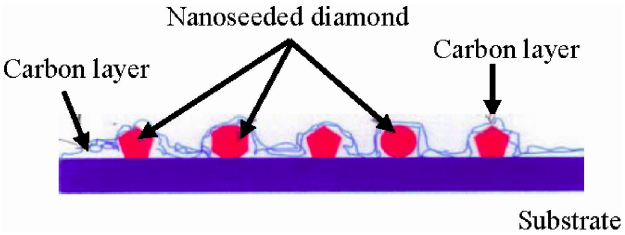

FIGURE 7. Schematic diagram of carbon layer on nanodiamondseeds.

The "screening effects" can be demonstrated in Fig.5 to show that, the equipotential lines and thus the electric field strength is different for one rod (or isolated rods) and three rods (placed near each other); the electric field strength becomes weaker when separation between the three rods becomes shorter. Thus in order to achieve high electric field strength the separation between the rods must be $\ell \sim 3\ell$ [5], where ℓ is the height of the rod. This indication shows that although rods with large aspect ratio would enable high concentrated electric fields, the use of such rods would limit the number of rods per unit area due to requirements for a $\ell \sim 3\ell$ separation between the rods.

Then the following equation represents the main parameters for maximization of the current density and hereafter we simply replace J phono by J or (3), based on optimization of the rod height and separation:

$$J \propto \alpha_{screening} NCrodEloc, (0 \prec \alpha_{screening} \leq 1) \quad (3)$$

Here, $\alpha_{screening}$ is a function of ℓ and N.

Based on the aforementioned parameters and discussions, we designed and fabricated electron emitter as described in the next section.

3. Design considerations for fabrication of carbon nano-materials for good emitters

The design approach was established by following conideration. Namely, let us suppose that there are two types of carbon nanotubes (CNTs) with the same diameters but differing length, $\ell_1 \sim \ell_2$. The CNTs are so arranged into two-dimensional arrays to satisfy that $\alpha_{screening} \sim 1$ is guaranteed or as shown in Fig.6.

For simplicity of the analysis, the separation (which should be $\ell \sim 3\ell_{1(2)}$) is made $\ell_{1(2)}$. The conductance of

the CNTs is inversely proportial to the height(ℓ) of the tubes to give a factor of ℓ_2/ℓ_1 difference and the β of the rods differs by a factor ℓ_1/ℓ_2. So, since the total number of protrusions differs by $(\ell_1/\ell_2)^2$, from (3), the emission current by the shorter rods, ℓ_2, is expect to be $(\ell_1/\ell_2)^2$ times larger than that by the longer rods, ℓ_1, assuming $\ell_1\ell_2$. If, for example, $\ell_1 \sim 1\mu$m and $\ell_2 \sim$ 100nm, then there is a factor of hundred difference in the magnitude of the current. Although this is a rough approximation of the configuration, we tried to prove this consideration and used a protrusion length of $\sim$100nm for the design and fabrication of electron emitters, as schematically shown in Fig.7.

Namely, at first 100 nano-diamond grains were deposited on a metal substrate or ITO electrode (cathode) on a glass substrate by the nano-seeding technique developed by us [6]. This seeding technique was originally employed for fabrication of diamond films at 200° by the magneto-active low pressure plasma CVD[6]. Next, room temperature cathodic arc deposition was used to deposit 10 $\sim$ 50nm thick conducting graphite-like sp^2 carbon films onto the nano-diamond to make protrusions to act as conductive rods. Then we succeeded to form electron emitters on glass substrates at room temperature [7].

4. Fabrication of electron emitters by Chemical Vapor Deposition(CVD)

Before explaining the emitters fabricated CVD to be described in this section, it may be worth mentioning about several favorable features of the carbon emitters. They are (a) sturdiness (from the fact that they can even be formed in a plasma); (b) high thermal conductivity (the current density in nano-structures is high, thus it is vital to have effective heat dissipation); and (c) fabrication of thin film nano-carbon emitters is rather easy. Then two kinds of emitters fabricated by CVD are explained below.

4.1. Silica Ball Emitter

As we reported already [8], Fig. 8 shows an array of commercially available silica balls (100 nm diameter)processed by following steps : (a) dispersion in ethanol; (b) spraying onto the surface of a high conductivity n++ Si substrate; (c) annealed at 60° to desorb the ethanol; (d) finally the hot filament method was used to deposit a graphite layer onto the array of silica balls to serve as the emitter.

Generally, the emitters are evaluated-although, to our knowledge, a definite agreement about the evaluation has not been made so far-as follows: (a) the threshold field (V/μm^{-1}) to produce a current density of 10μA/cm^{-2}; and,(b) the electric field (V/μm^{-1}) to achieve a current density of 1mAcm^{-2}, required for field emission displays (FED). Good electron emitters should exhibit the low threshold electric field. In the case of the present silica ball emitter, the values for (a) and (b) were 5 and 11μA/cm^{-2}, respectively. These characteristics was promising for carbon emitters when this report [8] was published in 2002.

4.2. Carbon nanowall emitters

Figure 9 shows thin films known as carbon nanowall (CNW) structures already reported by the present authors [9-11]. The CNW are thought to be composed of tens of layers of graphene sheets. And in Fig. 10, schematic illusrations of both CNT and CNW are presented for mutual comparison. As shown, these two structures are formed from nano-sized graphen sheets. Because these nano-sheets are energetically instable due to their high surface energies, the sheets tend to be stabilized by becoming into more stable forms like CNT and CNW. The fabrication of the CNW films[11] was performed by using a suitable metal substrate and DC or RF-CVD at 1000°. As seen in Fig. 9, the edge or wall separation is a few micrometers and it was concluded that the aforementioned conditions of screening effect are automatically satisfied, to provide sufficient concentration of the electric field.

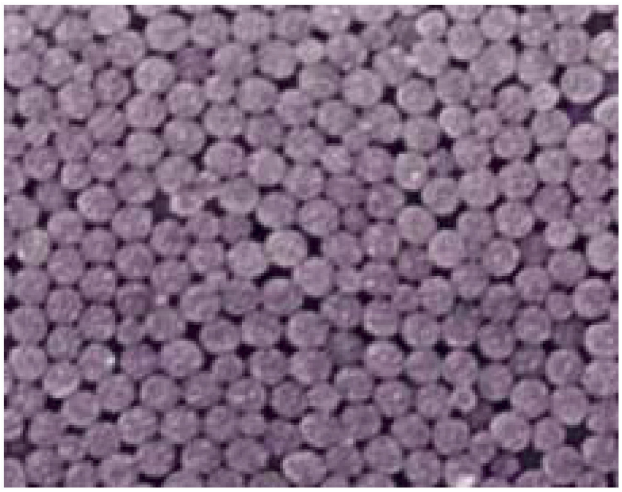

FIGURE 8. SEM image of silica spheres.

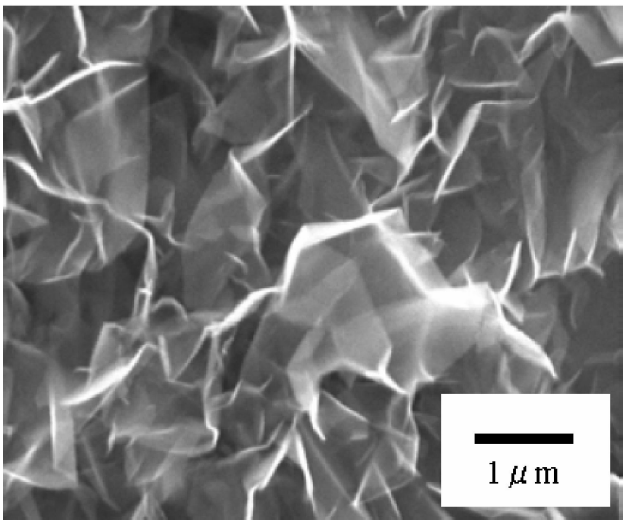

FIGURE 9. SEM image of CNW films.

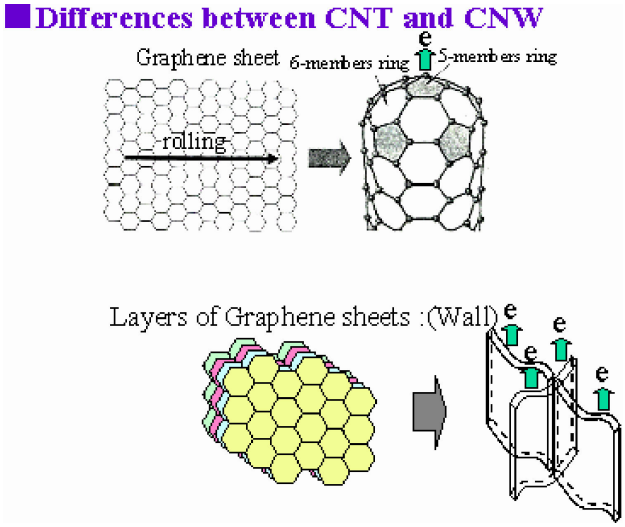

FIGURE 10. Schematic illustration of CNT and CNW.

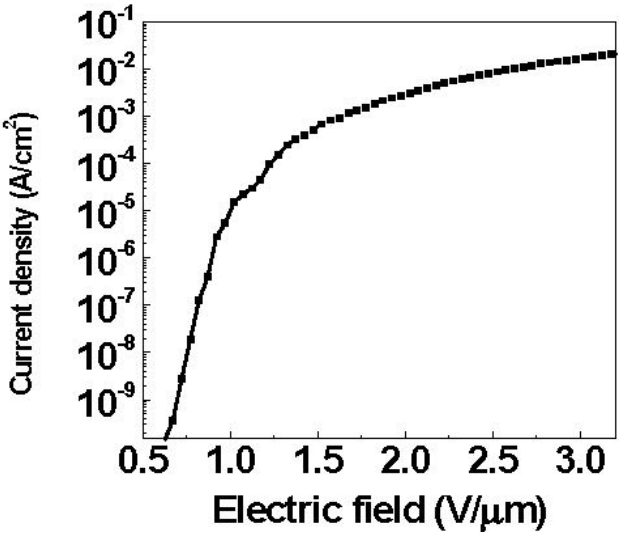

FIGURE 11. Field emission property of the CNW film.

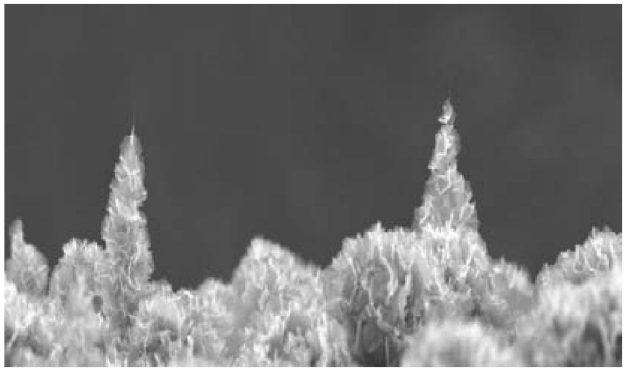

FIGURE 12. SEM image of CNX peaks in the area of CNW.

As shown in the characteristics of Fig.11, the resulting threshold electric field was reported to be 0.5 $\sim$1Vμm^{-1} and the field for achieving 1mAcm^{-2} is 1.5Vμm^{-1}[11], which implies an exceptional performance in comparison with our former emitters[7,8].

One possible reason of this far better quality of the CNW emitter is fabrication temperature. Because, it is easily expected that at the lower temperature, the higher contact resistance between the substrate and the graphinite rods may arise due to the weaker interface reaction. And in addition graphine rods treated at higher temperature can exhibit higher electrical conductance. However, recently far better improvement of the CNW emitter has been attained to be described in the next section. The key to the improvement is "An introduction of Carbon-Nano-eXit(CNW) structure into the CNW structure".

5. Improvement of CNW emitter due to CNX structure

During our study of electron emissivity of the CNW emitter, with respect to the CNW structure or morphology, we found, by chance, that an existence of small pyramid shaped protrusion in the area surrounded by the walls (CNW), as shown in Fig. 12, is essential for the electron emission. Then we have named the pyramid as CNX(Carbon-Nano-eXit) and claimed the patent. The formation process of the CNX is somewhat similar to the growth of one-dimensional(1D) nanostructure directed by use of a template [12], and in the present case CNW acts as a template or a scaffold as schematically illustrated by Fig. 13.

An excellent emissivity curve, plotted in linear scale to appreciate the emission current in -range, shown in Fig.14 was reported last year(2006), at the early stage of CNX study, to indicate that the threshold field to get 1mA/cm^2 emission current was 1V/μm and 109mA/cm^2 was obtained at 2.5V/μm[13].

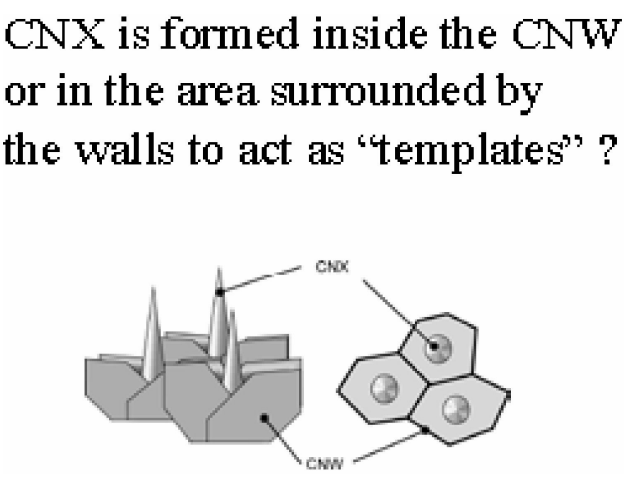

FIGURE 13. How CNX is formed?

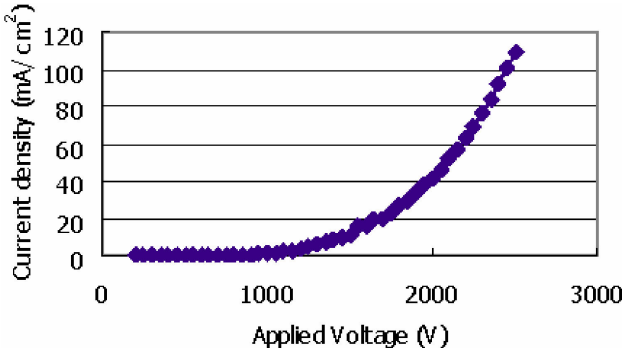

FIGURE 14. Field emission property of the CNX film.

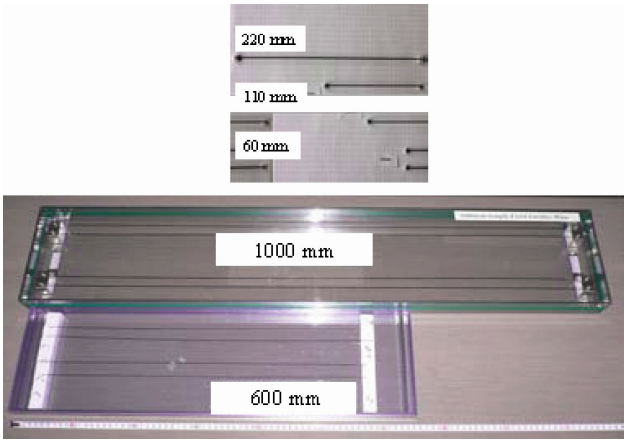

FIGURE 15. Wire-type Emitters with different lengths.

Then at present we are trying to fabricate emitter composed of mainly the CNX as fast as possible to correspond to mass production of good emitters. In this trial, we have found that CNX can be introduced into the emitter very rapidly by proper CVD technique(to be reported elsewhere soon). The emitters are of wire or pipe type (Fig.15) to avoid so-called "edge-effect". And so far, we are able to fabricate a world-top-ranking emitter with very low turn-on-voltage(0.5V/μm to induce 10mA/cm^2) and high emission current at low voltage with gap distance of 1mm(1mA/cm^2 at 1.1V/μm and 100mA/cm^2 at 2Vμm) in short fabrication time. Namely, we are able to produce about totally 50 $\sim$ 100km long good emitter per month by one CVD-reactor.

TABLE I.

1. Mercury-free to use low vacuum (10^{-4} - 10^{-6} Torr) in Lamps.
2. Extremely High Brightness.
3. Low electric power due to very high excitation efficiency by emitted electrons.
4. Instant lighting due to cold Cathode.
5. Low heat-emission.
6. Long-lifetime $> 10^4$hours.
7. Multi-color due to tailored mixture of phosphors.

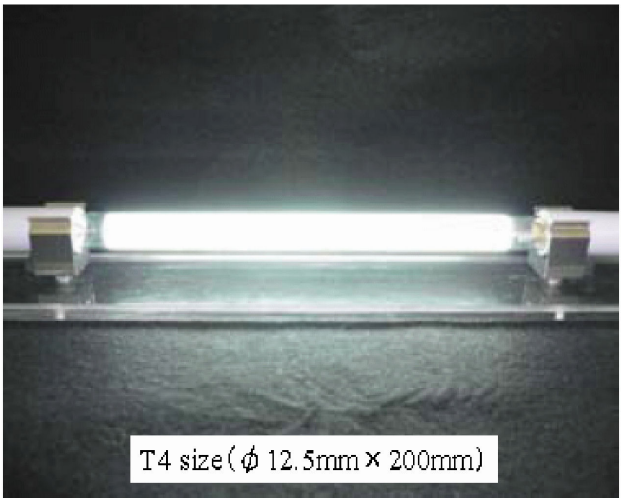

FIGURE 16. Typical FE lamp by our emitters.

6. Conclusion

It has been shown that an unique carbon-nano-structure named as CNX is very effective for fabrication of high quality electron-emitter. Since, the deposition or introduction of CNX structure on the metallic substrates(wire or pipe and even plate) can be done very rapidly, we can produce emitters in a mass production basis. There may be many ways of application of the emitter. At present we are trying not to employ emitters directly for display-pixels, but rather to fabricate large sized bright back-light lamp for LCD. The lamp or FEL(Field Emission Lamp)is of Mercury-free fluorescence type with high efficiency($\sim$60lm/watt) and high brightness of more than 10^5cd/m^2(white-light).

And then, in Table I some favorable features of FEL and in Fig.16, as one example, a very bright T4 sized lamp are demonstrated

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