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Derivation of length of carbon nanotube responsible for electron emission from field emission characteristics

Y. Gotoh,[a] Y. Kawamura, T. Niiya, and T. Ishibashi
Department of Electronic Science and Engineering, Kyoto University, Kyotodaigaku-Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

D. Nicolaescu
Ion Beam Engineering Experimental Laboratory, Kyoto University, Kyotodaigaku-Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

H. Tsuji and J. Ishikawa
Department of Electronic Science and Engineering, Kyoto University, Kyotodaigaku-Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

A. Hosono, S. Nakata, and S. Okuda
Mitsubishi Electric Corporation, 8-1-1 Tsukaguchi-Honmachi, Amagasaki, Hyogo 661-8661, Japan

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A method for deriving the length of carbon nanotube (CNT) in field emission arrays is proposed. Unlike the direct method of observation using a microscope, this method gathers information from functional measurements. Electron emission characteristics of CNT's printed on glass substrate were measured in a diode configuration. The macroscopic part of the voltage field conversion factor β was obtained from the relationship between the slope and intercept of the Fowler-Nordheim plot, and also from modeling of the electrodes. The length of the CNT was derived comparing the two values for β. The estimated length of the CNT agrees with direct measurements. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2740199]

Carbon nanotube (CNT) is expected to be a promising field emission cathode, due to its thin and long structure, together with the chemical inertness of the surface. Indeed, some of the device manufacturers have already demonstrated relatively large field emission displays based on CNT cathodes. The methods of fabricating CNT cathode are basically divided into two major groups: one method is printing paste that include CNT's on the substrate and the other is depositing CNT's directly onto substrate via, for example, chemical vapor deposition (CVD). The former method is inexpensive and applicable to industrial production, but the printed CNT paste generally shows low emission site density.

The emission site density may be increased by laser irradiation,[1] and also cyclic field emission test.[2] Such activation processes may cause explosion of the surface of the paste, resulting in formation of vertically standing CNT's. In most situations, we are obliged to evaluate the structure of the CNT's responsible for field emission through an observation with a scanning electron microscope (SEM) or a transmission electron microscope (TEM). This method, being destructive, cannot be applied to characterize modifications performed after fabrication of the display, such as the activation process of the CNT paste. If we can derive the length of the CNT from its functional electron emission properties, the obtained length should be that of the CNT responsible for electron emission. Therefore, the information will be useful because it is not necessary to break the sample. The present letter deals with derivation of the length of the CNT's from the field emission characteristics.

The samples were prepared in a following procedure. Paste involving CVD-CNT's was printed on a glass substrate coated with conductive indium tin oxide (ITO). The CNT paste was attached onto ITO layer by silane-coupling method. Raman-shift measurement of the samples indicated that the ratio of *G* peak to *D* peak was approximately unity, which implies that the samples were typical CVD-CNT's. Also, we confirmed through TEM observation that the CNT's contained in the sample are mostly capped multiwalled CNT's with a typical diameter of 20 nm.

Some of the samples were irradiated by KrF-excimer laser with the wavelength of 248 nm in air. The laser fluences were 86.4 mJ cm^{-2} (sample 2) and 704 mJ cm^{-2} (sample 3), and the pulse width was 20 ns. The treatment caused structural modification of the CNT paste to have isolated long CNT's with the length of 2–4 μm. The field emission test was done in ultrahigh vacuum ($<10^{-7}$ Pa) through our common procedure with a collector of tungsten etched needle.[3] Using such collector is convenient because we may restrict the origin of field emission to one or a few CNT's. We controlled the emitter (CNT)-collector spacing d_{EC} with a combination of mechanical motion drive and piezoelectric device. We applied a voltage V_{EC} between the emitter and the collector to have the emission current of, for example, 4 nA. We maintained the above current by controlling V_{EC} when we were approaching the collector toward the emitter by applying a larger voltage V_p to the piezoelectric device. Drawing a graph with V_p and V_{EC} for the abscissa and the ordinate, respectively, we can get the potential distribution between the electrodes. The origin was estimated by extrapolating the curve of V_{EC}. Prior to the measurement, the electron emission was stabilized for about 3–4 h by aging the sample. Approaching the collector toward the emitter from

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[a] Author to whom correspondence should be addressed; electronic mail: ygotoh@kuee.kyoto-u.ac.jp

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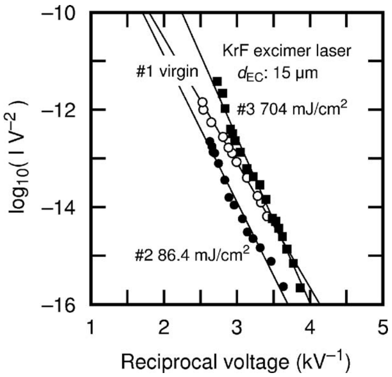

FIG. 1. Typcial FN plots of the electron emission properties of the CNT's with and without laser irradiation. The data were obtained at $d_{EC}=15$ μm.

30 to 1.5 μm, we measured the current-voltage (*I-V*) characteristics at different d_{EC}'s.

Figure 1 shows typical examples of the *I-V* characteristics of the CNT's with and without laser irradiation. The result was obtained for $d_{EC}=15$ μm. The characteristics are given in a Fowler-Nordheim (FN) plot. The open circles show the emission characteristics of the virgin sample (1), and solid circles and solid squares show those of the laser irradiated samples, 2 and 3, respectively. In this figure, the FN plot of the virgin CNT had a gentler slope as compared to those of laser irradiated CNT's. We measured *I-V* characteristics for several times and observed slight changes in the *I-V* characteristics. Consequently, FN plot also varied slightly. We analyzed the above variation with an aid of the Seppen-Katamuki (SK) chart. The SK chart is a two dimensional diagram taking as abscissa and ordinate the intercept and slope of FN plot, respectively.[4,5] Figure 2 shows the SK plots for the emission characteristics of the samples with and without laser irradiation. Same as Fig. 1, the open circles show the emission characteristics of the virgin sample (1), and solid circles and solid squares show those of the laser irradiated samples, 2 and 3, respectively. It is clearly shown that the FN characteristics are arranged as straight line for each sample, a typical result which has been already reported by many researchers.[6–9] It should be noted that the fitted line of the laser irradiated CNT showed a gentler slope. Here we define the absolute value of the slope of the SK plot as *A*.

The tendency of the other measurements made for different spacing d_{EC}'s was quite similar to the results described so far. Figure 3 shows the relationship between d_{EC} and *A*. The factor *A* is almost proportional to d_{EC}. The factor *A* is smaller for the sample irradiated with the higher fluence (3), larger for the sample irradiated with the lower fluence (2), and the largest for the sample without laser irradiation.

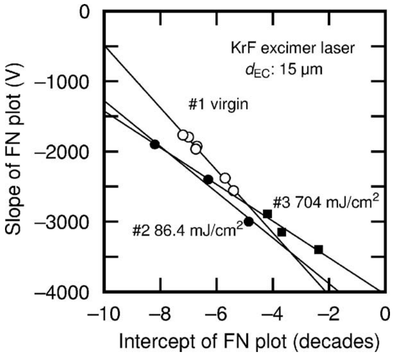

FIG. 2. SK (intercept-slope) plots of the electron emission properties of the CNT's with and without laser irradiation. The data were obtained at d_{EC} $=15$ μm.

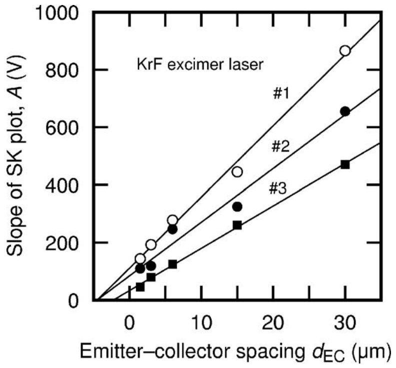

FIG. 3. Relationship between the electrode spacing d_{EC} and the factor *A*.

According to the present understanding of the SK analysis,[10] *A* gives approximate shape of the emitter and the slope is closely related to the voltage to local field conversion factor β. Generally, β can be written as

$$\beta = 1/kr, \tag{1}$$

where *r* is the apex radius and $1/k$ is the macroscopic component of β. The factor *k* is generally weakly dependent on *r*. The relation between *A* and physical parameters of the emitter is now considered to be

$$A = 0.95b\phi^{3/2}kr_n, \tag{2}$$

where *b* is a constant, ϕ is the work function, and r_n is a constant that is related to the emitter. The physical meaning of r_n has not yet been clarified. Considering r_n approximately $1/11-1/12$ of the apex radius, we can explain well the emission characteristics.[10] This finding was also confirmed recently by the authors using etched tungsten needles as field emitters.[11]

If the above hypothesis is true, then we can derive *k* from the experimentally obtained *A*, for specified value of ϕ for the CNT. Although the electron emission from CNT's may be localized to some specific sites,[12] here we treat the emission as uniform. The electric field at the apex of a thin long protrusion, with a base metal of which radius of curvature is large enough, is enhanced by a factor of $0.7h/r$.[13] Here *h* is the height of the protrusion. We confirmed the validity of the above expression through numerical calculations with OPERA3D/TOSCA software. The obtained field enhancement showed relatively good agreement with the above expression at $h=2$ μm and $r=10$ nm, although longer *h* gave slightly lower enhancement. SEM observation indicated that the density of the CNT that contributes to the electron emission is low enough to assure the following assumption: each CNT can be treated as an isolated protrusion on the substrate. In such a case, the electric field at the apex of the CNT *F* will be

$$F = \frac{0.7h}{r}\frac{V}{d_{EC}}. \tag{3}$$

From the above equation together with Eq. (1), we finally obtain

TABLE I. Derived length of the carbon nanotubes responsible for field emission.

Sample	A at 15 μm (V)	k		h (μm)	
		4 eV	5 eV	4 eV	5 eV
1	440	10.2	7.30	2.10	2.94
2	320	7.42	5.31	2.89	4.04
3	260	6.03	4.32	3.55	4.96

$$h = \frac{d_{EC}}{0.7k}. \tag{4}$$

From Eqs. (4) and (2), we can estimate h using experimentally obtained values for A. Table I denotes the estimated length of the CNT's, h. Here we used the A value at $d_{EC}=15$ μm. The CNT work function ϕ was assumed to be 4 or 5 eV, according to the spreading range shown in literature.[14,15] For r_n, a value of 0.83 nm was chosen because the CNT's have mostly a radius of 10 nm. The longest CNT's are obtained irradiating the CNT paste with higher laser fluence and the shortest CNT's are found in the virgin CNT. The obtained h values agree with the experimentally observed length of the CNT's, if the lower value $\phi=4$ eV for the work function is assumed.

The system used for the field emission measurements utilizes a sharp needle as a collector. Therefore, the electric field at the sample surface may be reduced compared to the case of a planar collector. We estimated the lowering of the electric field at the emitter surface, assuming that the collector is well approximated by a hyperboloid. Details of the analysis with such configuration can be seen in literature.[16] The result showed that the electric field will be reduced by a factor of $\ln(4d_{EC}/r_C)$ as compared to the parallel plate configuration, where r_C is the apex radius of the collector. Putting the values to this term, it is found that the field is almost half to one-fifth of the field corresponding to the parallel plate configuration. If this is applicable, the relationship between d_{EC} and V that gives the same F at the emitter surface will become a downward convex curve. Since V and A are closely related,[17] the relationship between d_{EC} and A will become a curve similar to that between d_{EC} and V. However, the d_{EC}-A diagram exhibited almost linear lines, and the parallel plate model may be applicable. This happens probably because the holder of the collector is large and the macroscopic figure of the electrodes may not be represented by a hyperboloid and a plate.

In conclusion, the lengths of the CNT's from laser irradiated CNT paste have been derived for different conditions and based on functional field emission measurements. Direct microscopic measurements have confirmed that the present method gives appropriate estimations for the length of the CNT's considered to be responsible for field emission. This method is applicable and useful for situations when the electrodes are well approximated by a parallel plate configuration. Although the estimates for the CNT length are rough, they are very useful for the functional evaluation of CNT arrays after different treatments.

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