Fabrication of Self-Aligned Nano-Structured Electron Emitters for Field Emission Scanning Electron Microscopy*

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Recent progress on aberration correction optics and single atom spectroscopy techniques increase needs of higher brightness electron sources than conventional single crystalline tungsten emitters. For this purpose, we are trying to fabricate a self-aligned nano-structured electron emitter using a field emission induced growth (FEIG) method in a field emission microscope (FEM) apparatus. The growth process can be monitored by the FEM, so that it is possible to control the nano-emitter size. A fabricated nano-emitter was mounted on a commercially available field-emission scanning electron microscope (FE-SEM) and its practicality was investigated. As compared with a carbon nanotube (CNT) emitter, the nano-emitter achieves larger beam current (better image contrast) and shows higher vibration durability. Emission stability of the nano-emitter is also within practical level, so that it was demonstrated that the FEIG nano-emitter could be a leading candidate for substituting conventional field emitters. [DOI: 10.1380/ejssnt.2014.192]

Keywords: Point electron source; Field emission induced growth (FEIG); Scanning electron microscopy (SEM)

I. INTRODUCTION

Recent progress on aberration correction optics and single atom spectroscopy techniques increase needs of higher brightness electron sources than conventional single crystalline tungsten emitters. There are several candidates for next-generation electron sources, one is a single-atom emitter [1] and another one is a carbon nanotube (CNT) emitter [2]. Single-atom emitters show the best performance in brightness and stability. However, it needs extreme-high vacuum and special electron optics with tilt mechanism, so that this emitter is limited to use for ultimate electron microscopy. While CNT emitters are more conventional and possibly be used for replacements of normal single crystalline tungsten field emitters.

We have been studied on CNT emitters fabricated by using manipulation method for use of field-emission scanning electron microscopy (FE-SEM). It has been reported [2, 3] that a CNT emitter has one to two orders of higher brightness than a tungsten emitter, and it can be used for a replacement of a normal tungsten emitter without any modification to an electron optics and a control system. However, there are several problems in CNT emitters. The most critical problem is that a beam current obtained from a CNT emitter is about 1/10 of a normal tungsten emitter with the same emission current. This reason is considered that electric field confinement at a tip of a CNT is very strong due to its large aspect ratio, so that electron emission from the tip diverges into large solid angle. The second problem is a beam alignment. Electron emission pattern from a CNT is strongly depends on its cap structure (positions of 5-membered rings), and it is almost impossible to control cap structures in atomic scale. For this reason, electron beam emitted from a CNT is tilted from its mechanical axis in most cases. Another problem is mechanical vibration. Because of its aspect ratio and flexibility, a CNT emitter easily vibrates, which results in vibration of focused electron beam.

To overcome these problems, an ideal point electron emitter should have a small emission area and less field confinement, in other words, a protrusion structure with a small radius and short length on a large curvature radius of a base material is optimum. However, this kind of structure is very difficult to realize by using a manipulation method of CNT. Thus, we choose a self-organized method to fabricate nano-structured electron emitter using a field emission induced growth (FEIG) method. The FEIG was initially reported as a fabrication method of aggregation of needle-like structures [4–6]. Yeong et al. demonstrated [7] that FEIG can be used to produce a single nanowire emitter. In our work, FEIG is carried out in a field emission microscope (FEM). Thus, growing emitter size can be monitored and controlled in real-time to obtain a nano-emitter suitable for an electron source of a FE-SEM. The grown FEIG emitters were also evaluated by using a commercially available FE-SEM.

II. EXPERIMENTAL

A polycrystalline tungsten wire with diameter of 0.15 mm was chemically etched to obtain a tungsten needle with tip radius of 300–500 nm. The needle was introduced into a FEM apparatus equipped with a gas introduction system. Base pressure of the FEM chamber was about 10⁻⁶ Pa. Fluorescent screen of the FEM was monitored by a digital still camera with movie recording capability. The screen was connected to a current detection resistance and the current was monitored by a handy oscilloscope system that is connected to a personal computer. The oscilloscope was also connected to a high-voltage power supply to monitor applied voltage and emission current simultaneously.

A FE-SEM system used in this experiment is a commercially available one (S-800; Hitachi Ltd.) without any modification to the electron optics or its control circuits. Base pressure of the gun chamber was much less than 10⁻⁷ Pa (monitored by an ion pump). The electron gun was operated under cold FE condition and target emission

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current was setup to $5 \mu A$. The acceleration voltage of the gun was selected as $20 \text{kV}$ for SEM image measurements.

III. RESULTS AND DISCUSSION

Figure 1 shows FEM pattern change during a FEIG process. The growth was carried out under $10^{-5} \text{ Pa}$ of residual gas pressure, and $4 \text{kV}$ of the FEM voltage was applied between the tip and the screen. Initially, many small spots appeared and disappeared as bubbles (Fig. 1(a)). After tens of seconds, a part of the bubble area became brighter (Fig. 1(b)), followed by rapid growth of the bright area (Fig. 1(c)). As compared with the concept of FEIG, these stages corresponds to, (a) adsorption and desorption of ionized gas molecules, (b) nucleation of a nano-protrusion at where electric field is most intense, (c) electric field confinement to the nano-protrusion and selective growth of the protrusion (see illustrations besides respective FEM patterns). It is also noteworthy that the bright spot appears on the central portion of the screen in most cases, which means the growth of the protrusion was self-aligned to optical axis of the base tungsten needle. If applied voltage is kept after the protrusion growth, emission current drastically increases up to tens of microamperes which results in breakup of the grown protrusion. Therefore, to use the nano-protrusion for electron emitter, the applied voltage should be stopped at appropriate growth stage. FEM patterns observed during a FEIG process under methane gas is basically the same as those under the residual gas. It is known that hydrocarbon components are always observed in mass spectra of residual gas. Therefore, it is considered that these hydrocarbon gases contribute to the FEIG process.

Figure 2 shows applied voltage and emission current during another FEIG process. In this experiment, $10^{-4} \text{ Pa}$ of methane gas was used. As shown by bold arrows A and B in the figure, emission current increases in spite of constant voltage, which indicates the growth occurs at these periods. Small arrows $a-g$ shown at the top of the Fig. 2 are time points where the voltage increases from $0 \text{ V}$ or decreases to $0 \text{ V}$. In other words, I-V measurements were carried out at these points and the results were shown in Fig. 3. Apparently, I-V curves $b$ and $c$, $d$ and $e$, $f$ and $g$ coincide each other at lower voltage ($<2.5 \text{kV}$), which is reasonable because the curve $c$...
(also e and g) was measured immediate after the curve b (also d and f) was measured. However, at higher voltage, curve e (or g) shows higher emission than d (or f), which means growth proceeds at higher voltage condition.

As mentioned above, noticeable growth occurred between a-b (‘A’ in Fig. 2) and e-f (‘B’ in Fig. 2), so that I-V curves can be grouped into three stages, (1) initial stage (a), (2) middle stage (b-e), and (3) final stage (f-g). Typical I-V curves (a, e, f) were chosen from respective stages and converted into Fowler-Nordheim (FN) plots, which are shown in Fig. 4. As shown in the figure, lower voltage region of the plots can be fitted by linear functions, while higher voltage region cannot be fitted, which is obviously caused by growth during I-V measurements. These fitted lines can be explained by FN theory as [8]

$$I/V^2 = \exp \left( \frac{9.8 \times 10^7 \phi^{3/2}}{\sqrt{\phi}} \right) + \frac{1.4 \times 10^{-6} \beta^2 A}{\phi},$$

where $A$, $\beta$ and $\phi$ are emission area, voltage-to-field conversion factor and work function, respectively. Therefore, it is possible to calculate $A$ and $\beta$ values from a slope and an intercept of a FN plot, if work function $\phi$ of an emitter is known. However, at present, material and composition (i.e. the work function) of the grown emitter is unknown. In this experiment, tungsten needle was used for base structure, and methane was used for source gas, so that it is assumed that grown emitter is made of tungsten, carbon or their composite. Respective work functions of tungsten, carbon nanotube and tungsten carbide are known as 4.4, 4.6 and 3.7 eV, thus the work function of the grown emitter was assumed between 3.7 and 4.6 eV for FN plot analysis.

Results of $A$ and $\beta$ analysis for respective growth stages are shown in Fig. 5. Two series of plots for $\beta$ correspond to $\phi=4.6$ eV and $\phi=3.7$ eV as indicated in the figure. Differences in $A$ plots for respective work functions were very small (in logarithmic scale), so that they are merged into one. From the $A$ and $\beta$ plots, $A$ decreased to 1/50 of the initial value, while $\beta$ increased to almost twice of the initial value. From these behavior of $A$ and $\beta$ values, it was confirmed that nano protrusion growth was occurred as illustrated in Fig. 1.

Obtained $A$ and $\beta$ values for FEIG emitter (at stage f) were compared with a commercially available single crystalline tungsten (SCW) emitter and a multi-walled carbon nanotube emitter (CNT). Values in parentheses are relative values to the CNT emitter.

$$\begin{array}{c|c|c|c}
\text{emitter} & \text{FEIG} & \text{SCW} [3] & \text{CNT} [3] \\
\hline
A \text{ nm}^2 & 15\sim16 (\sim 3) & 4.4\times10^4 (940) & 4.7 (1) \\
\beta \text{ cm}^{-1} & 3\sim4\times10^4 (\sim 0.07) & 2.4\times10^4 (0.05) & 5.1\times10^3 (1) \\
\end{array}$$

As for brightness, it has been reported that reduced brightness of a CNT emitter is one to two orders larger than that of a single crystalline tungsten emitter [3, 9, 10]. Although brightness of a FEIG emitter has not been measured at present, it is expected to be equal or larger than that of SCW emitter, and comparable to that of CNT. While for voltage-to-field conversion factor $\beta$, it is the same order as SCW emitter and less than 1/10 of CNT emitter. This means that the FEIG emitter has smaller emission area as a CNT but its field confinement is as same order as a tungsten emitter, which is an optimum structure for a point electron emitter as explained in the introduction above.

As for brightness, it has been reported that reduced brightness of a CNT emitter is one to two orders larger than that of a single crystalline tungsten emitter [3, 9, 10]. Although brightness of a FEIG emitter has not been measured at present, it is expected to be equal or larger than that of a CNT emitter because of the following reason. As shown above, an emission area of a FEIG emitter is larger than that of a CNT emitter by three times. While a beam current of a FEIG emitter obtained by using a commercially available FE-SEM was five times larger than that of a CNT emitter with the same aperture condition (see below for details). The reduced brightness of an electron source can be described as

$$B = \frac{I}{\Omega SV},$$

where $I$, $\Omega$, $S$, $V$ are a beam current, a solid angle of the beam, a vertical source size, and an applied voltage, respectively. With the same SEM electron gun, $\Omega$ and $V$ should be the same, and assuming that the vertical source

FIG. 4: FN plots for time points a, e and f in Fig. 3.

FIG. 5: Emission areas (A; open squares) and voltage-to-field conversion factors ($\beta$; filled circles) obtained from FN plots shown in Fig. 4. Broken lines in the figure are guide to eyes.

TABLE I: Comparison of emission area (A) and voltage-to-field conversion factor ($\beta$) between a field emission induced grown emitter (FEIG; this work), a single crystalline tungsten emitter (SCW), and a multi-walled carbon nanotube emitter (CNT). Values in parentheses are relative values to the CNT emitter.
size is proportional to the emission area, the brightness $B$ of the FEIG and CNT emitters are almost equal, or that of the FEIG is slightly larger than that of the CNT emitter.

Figures 6 and 7 show short and long term stabilities of emission current of (a) FEIG and (b) CNT emitters. Both of them were measured in the FE-SEM explained in the experimental section. Time duration for short time measurement was chosen as a time of a single SEM image acquisition, which is the minimum requirement for a SEM electron source. Long term duration corresponds to an usual measurement time for a single SEM experiment. For the short term stability (Fig. 6), both emitters almost kept constant in spite of many spike-like noises in the FEIG emitter. It is considered that the noise is caused by adsorption/desorption of gas molecules, and surface of FEIG emitter is more active than that of CNT. Fluctuation ratio of FEIG and CNT emitters are about 3% and 1% respectively. Practically speaking, 3% of fluctuation ratio is sufficient for SEM measurements because commercial FE-SEM systems usually have emission noise cancelation circuits which can eliminate several percent of fluctuations. While for the long term stability (Fig. 7), it is obvious that the FEIG emitter fluctuates and drifts largely than the CNT emitter. As shown in Fig. 7(a), FEIG emitter shows significant fluctuation for the first hour of emission followed by relatively stable state. This is a typical phenomenon for FEIG emitters, while CNT emitters always show stabilized emission from the beginning. During the large fluctuation, it is considered that the nano-protrusion of the FEIG emitter changes its shape to more stable structure (i.e. forming of the tip). After the forming process, the emission stabilized relatively within a practical level. However, this phenomenon is a potential problem of life time of the FEIG emitter, so that it should be solved in the further research.

Finally, SEM images taken by a FEIG emitter and a CNT emitter were compared (Fig. 8). Observed sample is a standard sample for SEM resolution evaluation (Au particles on graphite). The image resolution is similar to each other, but it is obvious that image contrast using the FEIG emitter is much better than that using the CNT emitter. Respective beam currents (measured at the bottom aperture) obtained from the FEIG and the CNT emitters were 4.6 nA and 0.9 nA respectively for the same emission current target of 5 $\mu$A, and the larger beam current causes image contrast ($S/N$ ratio) improvement. As shown in Table I, FEIG emitter has small $\beta$ (or less electric field confinement at the tip), which suppress electron emission divergence angle and results in increase of beam current. It is also shown that noises caused by vibration of the CNT emitter (see magnified image of (b); edge of gold particles looks zigzag) is almost vanished in the image taken by the FEIG emitter, which proves that the FEIG emitter is much vibration tolerant than the CNT emitter. As mentioned above, FEIG emitters are self-aligned to an optical axis, so that alignment operation of electron gun of the FE-SEM is much easier than that of CNT emitters, i.e., all of the FEIG emitters (8 of 8 samples) successfully aligned to obtain electron beam at sample position, while less than 20% of CNT emitters (2 of 12 samples) succeeded for alignment. This is also an advantage for use in existing FE-SEM systems.
IV. CONCLUSION

Self-aligned nano-structured electron emitter was fabricated by using a field emission induced growth method in a gaseous FEM, and the grown emitter was evaluated by using a commercially available FE-SEM. It was proved by I-V analyses of growing emitter that nano protrusion structure was grown on relatively large curvature radius of tungsten tip. The FEIG nano emitter has an emission area as same order as that of a CNT emitter, and also an voltage-to-field conversion factor as same as that of a normal tungsten field emitter. Because of small voltage-to-field conversion factor, the FEIG emitter achieved higher beam current than the CNT emitter, which resulted in SEM image contrast enhancement. It was also confirmed that the FEIG emitter is much vibration tolerant and easier for alignment than the CNT emitter. Although a problem on long term emission stability remains, it was proved that the FEIG emitter is a promising candidate for brighter point electron source.

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[1] T. Ishikawa, T. Urata, B. Cho, E. Rokuta, C. Oshima, Y. Terui, H. Saito, and T. T. Tsong, Appl. Phys. Lett. 90, 143120 (2007).
[2] H. Nakahara, S. Ishikawa, T. Ochiai, Y. Kusano, and Y. Saito, e-J. Surf. Sci. Nanotech. 9, 400 (2011).
[3] H. Nakahara, Y. Kusano, T. Kono, and Y. Saito, Appl. Surf. Sci. 256, 1214 (2009).
[4] H. B. Linden, E. Hilt, and H. D. Beckey, J. Phys. E 11, 1033 (1978).
[5] F. Okuyama, J. Appl. Phys. 53, 6226 (1982).
[6] F. Okuyama and Y. Fujimoto, J. Appl. Phys. 56, 566 (1984).
[7] K. S. Yeong, J. B. Law, and J. T. Thong, Appl. Phys. Lett. 88, 193116 (2006).
[8] J. Ishikawa, H. Tsuji, K. Inoue, M. Nagao, T. Sasaki, T. Kaneko, and Y. Gotoh, Jpn. J. Appl. Phys. 32, L342 (1993).
[9] N. de Jonge, M. Alliouz, J. T. Oostveen, K. B. K. Teo, and W. I. Milne, Phys. Rev. Lett. 94, 186807 (2005).
[10] K. Hata, A. Takakura, A. Ohshita, and Y. Saito, Surf. Interface Anal. 36, 506 (2004).