Electron Microscopic Observations of Field Emission from a Carbon Film Composed of Graphite Sticks

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A carbon film composed of graphite sticks as field emission (FE) points is studied using field/photoemission electron microscopy (F/PEEM) and scanning electron microscopy (SEM). The film is termed an ND/CNW film since nano-crystalline diamond is grown over a carbon nano-wall layer in the film. It was found that about 8% of graphite sticks present on the ND/CNW film work as field emitters. The sizes and postures of the three representative graphite sticks that work as field emitters are determined by SEM observations. The time dependence of the FE current of the single emission sites was measured by FEEM at a field of 1.0 V/μm. The average FE current from a single emission site at the field of 1.0 V/μm is found to be 10–100 nA. The time dependence of the FE current was compared with those of FE currents of other carbon nano-materials. The results suggest that the cause of FE fluctuation is adsorption and desorption of molecules on the emission site, indicating the reason for the prolonged FE lifetime of the graphite sticks on the ND/CNW films. [DOI: 10.1380/ejssnt.2011.176]

Keywords: Field emission microscopy; Graphite; Nano-films; Nano-crystalline diamond; Carbon nano-walls

I. INTRODUCTION

Field emission (FE) from nanoscale materials has become the focus of extensive studies due to its importance in the fabrication of vacuum electronic devices, such as field-emission flat panel displays, X-ray sources and microwave devices. FE from nanoscale materials relies on the so-called field enhancement at a sharp tip of the nanoscale material. Nanoscale materials used for FE range from carbon nanotubes (CNTs) [1, 2] to various nanostructures of oxides [3–6]. FE from nanoscale forms of carbon sheets obtained using chemical vapor deposition (CVD) has also been attracting significant attention [7]. It has been shown that a carbon film, a nano-crystalline diamond film grown over a carbon nano-wall layer (ND/CNW film), has excellent field emission characteristics (larger than 1 mA/cm² at 1 V/μm and a lifetime (time when the emission current decreases to half of the initial value) of more than 10⁴ h) [8, 9]. The current density of 1 mA/cm² yields sufficient brightness with a typical high-voltage phosphor screen efficiency [1]. To the best of the authors’ knowledge, FE characteristics superior to that of 1 mA/cm² at 1 V/μm have been reported only in three cases, (1) FE from ZnO nanowires grown on carbon cloth (1 mA/cm² at 0.7 V/μm) [10], FE from CNTs grown on carbon cloth (1 mA/cm² at 0.4 V/μm) [11] and (3) FE from silicon nanowires grown on carbon cloth (1 mA at 0.7 V/μm) [12].

The origin of field emission from ND/CNW films was recently examined by field emission spectromicroscopy and scanning electron microscopy (SEM) [13]. It was found that graphite sticks were present at the field emission sites on the film. Energy distribution curves of the field-emitted electrons had the same features as those of field-emission from a metallic substance (graphite). It was thus concluded that graphite sticks present on the ND/CNW film are responsible for the field emission. In this study, details of the field emission characteristics are reported, in particular (1) the percentage of active emission sites on the graphite sticks on the ND/CNW films, (2) mean field emission current from a single emission site, and (3) time dependence of the field emission current of the single emission site. These results are discussed and compared with FE from other nanoscale materials.

II. EXPERIMENTAL

The samples investigated in this study were made using a DC plasma CVD system. Si(001) wafers with an area of 6×6 mm² were used as substrates. Prior to the CVD deposition, the substrates were exposed to a hydrogen plasma for 5 min to remove any oxide layers or contaminants. During the deposition, hydrogen gas mixed with 10% CH₄ gas was introduced into the growth chamber, and the substrate temperature was controlled at about 1000°C by changing the DC current. The total gas pressure during CVD deposition was 70 Torr and the growth time was 4 h. These growth conditions were optimum in terms of field emission characteristics, and similar to those reported in Ref. [8].

The field emission characteristics (FE current vs. electric field (I–V)) of the samples were measured using a parallel-plate diode device with a cathode-anode spacing of ~5 mm. All the samples showed FE currents of ~2 mA/cm² at 1.0 V/μm. Field/photoemission electron microscopy (F/PEEM) observations were carried out using a commercial system (Omicron FOCUS IS-PEEM) comprising electrostatic lenses and an electron energy analyzer. A ~6×6 mm² piece of each sample was placed in the Mo holder of the microscope. Micro-spot electron energy analysis of field/photoemitted electrons was possible...
at a maximum spatial resolution of \( \sim 1 \) \( \mu \)m using an iris aperture placed on the first image plane. The spatial resolution of the emission microscope was \( \sim 20 \) nm and the base pressure of the apparatus was \( \sim 6 \times 10^{-11} \) mbar. For PEEM, a Xe discharge lamp (Hamamatsu L2174) with a maximum photon energy exceeding 6.2 eV was used. The distance between the sample surface and the front end of the objective lens electrode (extractor electrode) was about 1.8 mm. The sample could be electrically biased to have a negative voltage so that electrons with low kinetic energies could be analyzed for microspectroscopy. The energies of emitted electrons were expressed with respect to the Fermi level \( (E_F) \) of the sample holder, which was determined from the so-called \( E_A \) peak [14] of colloidal graphite (Aquadag) pasted on a different place on the sample holder and excited using an electron beam at an energy of 3.7 kV.

FIG. 1: SEM image of the side of the ND/CNW film which was intentionally cracked around the middle.

FIG. 2: Mosaic PEEM image of the ND/CNW film. Eight small PEEM images were combined to form this mosaic. Each small image was obtained at an extractor electrode voltage of 160 V (\( \sim 0.08 \) V/\( \mu \)m).

FIG. 3: Examples of individual PEEM images. a) and c) are images under an extractor voltage of 160 V with different areas, and b) and d) are images of the corresponding areas under the extraction voltage of \( \sim 1600 \) V (\( \sim 0.8 \) V/\( \mu \)m). The locations of some of the graphite sticks appear as dark ‘flower’ patterns and are marked with red arrows. Bright dots appearing at the centers of some of the ‘flower’ patterns in b) and d) are field emission points.

III. RESULTS

Figure 1 shows a typical SEM image of the side of a sample which was intentionally cracked around the center. It shows graphite needles (single crystals with the c-axis perpendicular to the needle orientation [8, 13]) in a variety of forms sticking out of the agglomerates (few micrometers in size) of nano-crystalline diamonds.

Figure 2 shows a mosaic PEEM image of a sample which was prepared by combining 8 small PEEM images. Each small image was obtained at an extractor electrode voltage of 160 V (\( \sim 0.08 \) V/\( \mu \)m) [15]. In Fig. 2, the large dark areas on the left and upper parts are regions where colloidal graphite paste (Aquadag) was painted as location markers and to negate active FE sites. In the bright regions outside the dark colloidal graphite areas, mountain-like features appear to be distributed randomly; these are large agglomerates of nano-diamonds. Shadows of the mountain-like features are on the left side since the excitation Xe-light is from the right at an incident angle of \( \sim 30^\circ \) from the surface. The locations of the graphite sticks are rather difficult to identify in this mosaic image, but they are the slightly darker areas marked with circles. The red circle indicates the location of the graphite stick that showed field emission, as will be explained later, and the white circles are the locations of graphite sticks that showed no field emission under the extractor voltage of 2,000 V (\( \sim 1.0 \) V/\( \mu \)m).

Examples of the individual PEEM images are shown in Fig. 3. Figures 3a) and 3c) are PEEM images under an extractor voltage of 160 V, and Figs. 3b) and 3d) are PEEM images of the corresponding areas under an extraction voltage of \( \sim 1600 \) V (\( \sim 0.8 \) V/\( \mu \)m). The locations of graphite sticks appear as dark ‘flower’ patterns (some are marked with red arrows) since distortion of the electric...
FIG. 4: a) Typical time dependence of the total FE current for a period of ∼30 min from the three FE points of FE1, FE2 and FE3 at a field of 1.0 V/µm. The data points of the curve are shown with small open circles every 1 s and each datum point is connected by solid lines. b) Typical time dependence of the FE current of each FE point of FE1, FE2 and FE3 at a field of 1.0 V/µm.

field occurs yielding a darker appearance in the PEEM image [13]. As the extractor voltage is increased, as in Figs. 3b) and 3d), bright dots appeared at the centers of some of the ‘flower’ patterns. These bright dots are locations of field emission since they remained even when the Xe-lamp was turned off; the brightness was very dependent on the extractor voltage. We found three FE points around this area, labeled FE1, FE2 and FE3 in Figs. 3c) and 3d). The FE1 position can be seen in Fig. 2 marked by a red circle, and FE2 and FE3 were present somewhere outside the region shown in Fig. 2.

We searched an area of ∼1.8 mm² on the sample surface under an extractor voltage of 2000 V and found 8 FE points and about 92 non-FE points. Although the numbers of FE and non-FE points found are not sufficiently large for good statistical analysis, we conclude that about 8% of the graphite sticks operated as field emitters in this sample, and the number densities of FE and non-FE graphite sticks were ∼4/mm² and ∼51/mm², respectively. Since the FE points were specifically counted, the number density of FE points is more definite. The distribution of the FE points appeared to be random. The number density of ∼55/mm² of the total graphite sticks is roughly consistent with the number density of major graphite sticks observed in the SEM images. For other samples formed under the same growth conditions, the percentage and number density of FE points are expected to be about the same since the FE current density as measured by the parallel-plate diode device was about the same.

The area of the ND/CNW film was further covered by the colloidal graphite paste to leave a limited open area of just 0.07 mm². This was done to negate some of the FE sites. Only three FE points (FE1, FE2 and FE3) were left in this limited area. The time dependence of the total field emission current (due to the three FE points) was monitored by measuring the sample current under an extraction voltage of 2000 V (∼1.0 V/µm) without Xe-lamp excitation. Figure 4(a) shows typical time dependence of the total field emission current for a period of ∼30 min. The data points of the curve are shown with small open circles at every 1 s and each datum point is connected by solid lines. The curve shows instantaneous (within the sampling time of 1 s) changes in the current of 20% together with a transient rise in the current of 10%. The time dependence of the FE current of individual FE points was further measured by measuring the time-dependent FEEM images at a frame rate of 1 s at a field of 1.0 V/µm. In this case, the detector (micro-channel plate detector) voltage of the image screen was reduced to a low value to maintain a linear response of the electron intensity. The result is shown in Fig. 4b). The electron intensity (in nA) on the ordinate is estimated from the time-averaged fraction of the field emissivity of the three FE points as FE1:FE2:FE3 = 0.6:0.3:0.1. The time on the abscissa for the FE1 point is the same as in Fig. 4a) but the time for
the graphite sticks at the FE1, FE2 and FE3 points were paratus and installed in an SEM apparatus. The shapes of later.

Possible reasons for the current changes will be discussed
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an FE current of
is caused by the current change of FE2. It can thus be
that the transient rise in the current of 10% in Fig. 4a) is
caused by the change in currents of FE1 and FE2 and
instantaneous change in current of 20% in Fig. 4a) is
It can be seen in Fig. 4 that an instantaneous change in
the FE2 and FE3 points is different from that of Fig. 4a).
It can be seen in Fig. 4 that an instantaneous change in
current of 20% in Fig. 4a) at the time of around 3.6 min is
classified due to the boundary of the agglomerates (few µm size) of the nano-diamonds.

The graphite stick at FE1 has a special shape wherein
a shorter stick supports the other longer stick. Graphite
sticks at FE2 and FE3 have a simple straight needle-like
shape. The diameter of the ‘foot’ of the longer stick at
FE1, and those at FE2 and FE3 were determined from
other SEM images to be ~60 nm. The shapes and di-
diameters at the tips of the graphite sticks could not be
determined due to mechanical vibration of the tips.
The lengths and postures of the three sticks were examined
by SEM imaging from different directions. The length
of the longer stick at FE1 was found to be 29 µm with
the mean direction tilted by 15° from the surface normal.
The lengths and tilt angles of the sticks at FE2 and FE3 were
found to be 37 and 36 µm and 6° and 3°, respect-
ively. Thus, it can be stated that the graphite sticks
that show good field emission properties have a length
of about 30 µm and stand almost normal to the film surface.

IV. DISCUSSION

In previous I–V measurements of several individual
field emission sites, it was found that the field emission
is indeed of the Fowler-Nordheim (FN) type and that the
field enhancement factors ($\beta$) evaluated from the slope of
the FN plot, assuming a typical work function of graphite
of 4.5-5.0 eV, were ~2000 [13]. The field enhancement
factor of a conductive cylindrical rod (vertical to a flat
conductive substrate) with a length $L$ and hemispheri-
el end with radius $R$ was numerically evaluated to be
$\beta = 1.2(L/R + 2.15)^{10.9}$ [1]. By substituting the typical
present values of $\beta = 2000$ and $L = 30 \mu m$ in this equa-
tion, we obtain $R = 7.9 \mu m$. Although the size of the
tips of the graphite sticks in the present work could not
be experimentally determined due to mechanical vibra-
tion of the sticks, we can assume that the size of the tips
of the graphite sticks is around the order of ~8 nm. The
mean FE current of 10-100 nA out of the tip with a size
of ~8 nm deduced for the present graphite sticks is suf-
ficiently small for the graphite sticks to be durable when
compared to the typical FE currents on the order of µA
from CNTs [2].

The time dependence of the FE current shown in Fig. 4
has a resemblance to the time dependence of the FE cur-
rent from glassy carbon tips (Fig. 7 of Ref. [16]) and from
CNTs (Fig. 3 of Ref. [17]) measured at RT. It was re-
ported [16, 17] that the fluctuation of the FE current
is drastically reduced when the tip temperature was in-
creased to more than ~900°C. From the temperature de-
pendence and stochastic analysis of the fluctuation of
FE current from graphene nano-needles, Matsumoto et al. [18],
reported that the fluctuation is due to adsorption
and desorption of molecules onto the emission sites
(possibly on the basal plane of the graphene sheets) and
that the adsorption energy can be evaluated to be 45 meV

http://www.sssj.org/ejsnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejsnt/)
for H$_2$ molecules. From an analysis of FE current fluctuations as a function of temperature, FE current, introduced gas species and gas pressure, Yamamoto et al. [16] concluded that the fluctuation of FE from glassy carbon tips is caused by dislodgement of adsorbed molecules by impinging ions that are formed near the tip surface by the FE current. It is worth stressing that the proposed origin of the FE current fluctuation does not cause distortion of the tip structure itself, rather, it results in simple adsorption and desorption on the graphite tips. A similar scenario may be conjectured for the present FE from graphite sticks since the time-dependence of the FE current from the individual graphite sticks bears a resemblance to the time-dependence of the FE current from glassy carbon tips [16], CNTs [17], and a prolonged lifetime of more than $10^4$ h is achieved in a poor vacuum condition of $10^{-3}$ Pa [9]. It is worth mentioning here that mechanical vibration of the graphite sticks, as observed in the present study, cannot cause the fluctuation in the FE current which is basically ‘electronic’ in origin. It should also be mentioned that the presence of ND/NCW films under the graphite sticks may have no characteristic effects on the excellent and prolonged nature of FE, but rather provides a stable and conductive support for the graphite sticks. To the best of the authors’ knowledge, there is no previous report of graphite sticks of this sort distributed over a stable and conductive base.

V. CONCLUSION

By detailed observations using P/FEEM and SEM of carbon films composed of graphite sticks as field emission sites, the percentage of active emission sites from the graphite sticks was found to be $\sim$8% and the mean field emission current from a single emission site was 10-100 nA for a field of 1.0 V/µm. From observations of the time-dependence of the field emission current of a single emission site and from comparison with the time-dependence of the FE current for other carbon field emitters, we suggest that the cause of FE fluctuation is adsorption and desorption of molecules on the emission site. This may be the reason for the prolonged life time of the present field emitter, the graphite sticks on ND/NCW films.

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