Estimation of emission field and emission site of boron-doped diamond thin-film field emitters

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The electric field required to emit electrons for boron-doped diamond together with the emission site was estimated using measurement systems that can precisely control the emitter–collector gap and lateral position. Three different types of field emitters were prepared by microwave plasma chemical vapor deposition. Type A was a typical diamond film on a flat silicon substrate, type B was a heteroepitaxial diamond film that was deposited on a (111) oriented platinum substrate, and type C was a pyramidal diamond film fabricated by the transfer mold method. For all the emitters, the voltage required to extract 0.2 nA was measured as a function of the emitter–collector gap, where the device of the emitter–collector configuration is approximated by a pair of parallel plates. The results showed that a strong electric field was applied in front of the emitter. For type B, the emission current distribution was measured by a device in which the collector was an etched needle. It was found that the emission current was concentrated at some points, which would be the crystallite edge, and also that, even at a flat crystal facet, electrons were emitted by applying a similar electric field. A similar result was obtained for type C emitters. This study revealed that the electron can be emitted from any position on the film, but generally the crystallite edge is the most probable emission site due to the concentration of a high electric field there compared to other places on the film. © *2000 American Vacuum Society.* [S0734-211X(00)03402-8]

I. INTRODUCTION

Diamond and diamond-like carbon films are of great interest for their superior electron emission property with very low threshold voltage,[1–3] and extensive research on them is currently taking place.[4] Although many researchers have investigated the emission property from diamond related materials, including a theoretical approach,[5] the mechanism of electron emission is not clarified as yet. This is entirely due to the fact that most of the measurements have been performed using a simple diode structure, and the electric field is calculated assuming the emitter–collector is a parallel-plate system. However, diamond thin films have unique texture due to crystal habit so it is not expected that a uniform electric field would be applied to the diamond film surface. We have already reported that the emission characteristics of boron-doped diamond thin-film field emitters depend on the morphology of the film.[6] Measurements in a sandwich structure often cause an unexpected high field[7] and are misleading to the experimental results. Thus, in order to clarify the electron emission mechanism, a very careful investigation is necessary. So far, few attempts have been made to elucidate the absolute value of the emission field.[8–10] The purpose of the present study is to determine the electron emission field and electron emission site to provide useful information for the analysis of the emission mechanism from diamond thin-film field emitters.

II. SAMPLE PREPARATION

As described above, the texture of the film is closely related to the emission property, thus, in this study, three different types of diamond thin-film field emitters were fabricated by microwave plasma chemical vapor deposition (MPCVD). Details of the deposition parameters are listed in Table I. Figures 1(a)–1(c) show the scanning electron micrographs [(SEM) images] of fabricated emitters of types A, B, and C, respectively. Details of the preparation of these emitters are described below.

A. Type A emitter: Typical CVD diamond film

The type A emitter was deposited on a flat silicon (Si) substrate. Details of this sample are reported elsewhere[11] and we only describe the deposition process briefly. MPCVD was performed with a 0.5% methane–hydrogen mixture, with the addition of diborane gas of 1 and 10 ppm. The substrate temperature was 800 °C. The surface was terminated by oxygen by dipping the sample into boiling chromic acid and subsequently into boiling aqua regia. The sample was cut and one piece of it is used as an oxygen terminated (O-terminated) emitter, the other was treated in hydrogen plasma and used as a hydrogen terminated (H-terminated) emitter. The typical grain size of these films is 1–2 μm. Details of the emission properties of these films were already reported elsewhere.[6,12]

B. Type B emitter: (111) oriented heteroepitaxial flat film

The type B emitter was heteroepitaxial diamond on a (111) oriented platinum substrate.[13,14] Deposition was per-

TABLE I. Deposition conditions for type A, B, and C emitters.

Condition	Type A (typical)	Type B (heteroepitaxial)	Type C (pyramidal)
Substrate	p-Si(100)	Pt(111)	Si(111) facet of Si(100) mold
Substrate temperature	800 °C	875 °C	800 °C
Methane/hydrogen ratio	0.5%	0.3%	0.5%
Diborane concentration	1, 10 ppm	10 ppm	1, 10 ppm
Deposition time	12 h	30 h	12 h
Surface treatment	H and O terminated	H terminated	⋯

formed with a 0.3% methane–hydrogen mixture. Ten ppm of diborane gas was added to the plasma. The substrate temperature was 875 °C. Deposition lasted for 30 h and after that the sample was exposed to hydrogen plasma to obtain a hydrogen-terminated surface. The resultant film showed a (111) orientation but intensive coalescence of the grain boundaries was seen and the film texture was almost flat. The edge of the crystallites has a step of a few hundred to thousands of nanometers according to the SEM image. The size of the grains reaches several μm.

C. Type C emitter: Pyramidal diamond film

The type C emitter was 4 μm high pyramidal diamond array fabricated by the transfer mold method.[15] First, the surface of a (100) oriented Si substrate was thermally oxidized to a thickness of 1 μm. Positive-tone photoresist was spin coated on and a pattern that consisted of a 64×64 array of 3 μm circles was transferred. The pattern was developed and a SiO$_2$ layer was etched by buffered hydrofluoric acid to form 4096 holes. A Si mold was fabricated by unisotropical etching in tetramethylammoniumhydroxide (TMAH). After removing the oxide layer, diamond was deposited under similar conditions to those of the type A emitters. The sample was held on a glass plate with conductive paste, and finally the Si mold was removed by a combination of mechanical and wet etching. The presence of tetrahedral bonding was confirmed by x-ray photoelectron spectroscopy (XPS).

III. MEASUREMENT OF ELECTRON EMISSION CHARACTERISTICS

A. Measurement system

In order to determine the emission field and emission site of the diamond thin-film field emitters, two different systems were used. These systems are shown schematically in Figs. 2(a) and 2(b). Figure 2(a) shows a parallel-plate system which consists of a diamond film emitter and a gold ball collector.[6,12] The emitter is held on the plate which can be moved by a piezoelectric device (z piezo) along the direction perpendicular to the emitter surface (z direction). The collector is mounted on a mechanical linear drive and can be moved also along the z direction. Since the diameter of the gold ball is approximately 2 mm, the emitter–collector ge-

ometry is approximated by parallel plates when the gap is reduced to submillimeters. This system was used to estimate the emission field.

Figure 2(b) shows a point measurement system that consists of an etched needle collector and an emitter holder that can be moved along the lateral directions (x and y directions). For this system, the collector is mounted on the mechanical linear drive by a piezoelectric device (z piezo). The collector was electrochemically etched 0.1 mm tungsten wire. The apex radius of the needle was less than 1 μm. The emitter holder is also fixed to a base by two piezoelectric devices (x and y piezos) in order to move along the lateral direction. In the present study, the same voltage was applied to the x and y piezos and a one-dimensional scan was performed.

The measurement system was installed into a vacuum vessel that is pumped by a sputter ion pump and a titanium sublimation pump. The residual gas pressure during the measurement was about 10^{-7} Pa. All the measurements were performed after aging the sample for several hours to stabilize the emission current.

### B. Measurement of emission field

The emission field was investigated using the parallel-plate system for all the emitters. The spacing between the emitter and the collector (d_{EC}) was adjusted by the z piezo. To obtain the emission field, an easy way is to obtain the potential distribution $\Phi(d_{EC})$. In order to measure Φ between the emitter and the collector, we measured the voltage required to extract 0.2 nA (V_{th}) as a function of d_{EC}. If the emission area does not change significantly, keeping the emission current constant means keeping the electric field at the emission site constant. That is, the voltage curve provides a potential distribution. The electric field at the point can be derived by differentiating $\Phi(d_{EC})$. Figure 3(a) shows the relation between $V_{th}(=\Phi/e)$ and d_{EC} for type A emitters. The characteristics illustrated here are for the samples deposited with 1 ppm diborane and both H and O terminated. The dashed line indicates a similar relation obtained by a conventional nickel deposited field emitter.[16] For the etched field emitter, the potential curve shows an upward convex trend, and the slope of the curve becomes steeper at the emitter surface. For the diamond thin-film emitters, however, the Φ is almost a linear line at a point away from the emitter, unlike the conventional field emitter. In this region, the
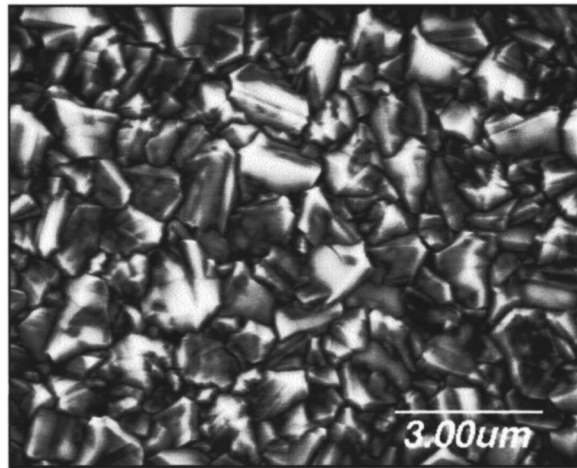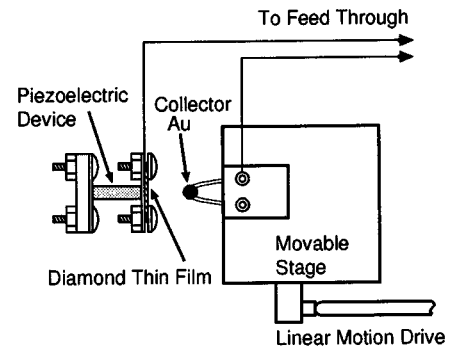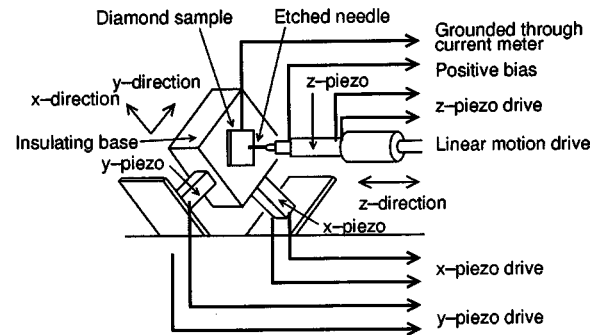
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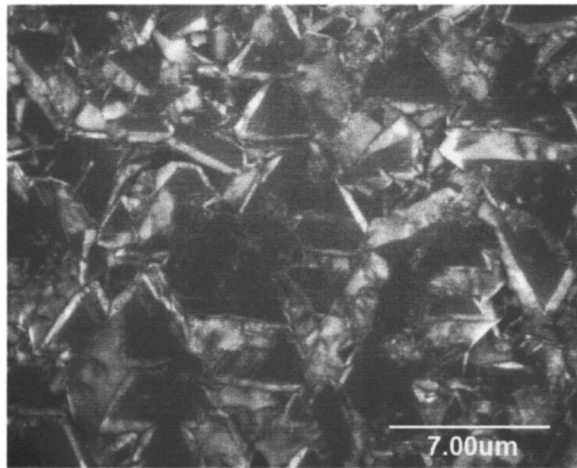
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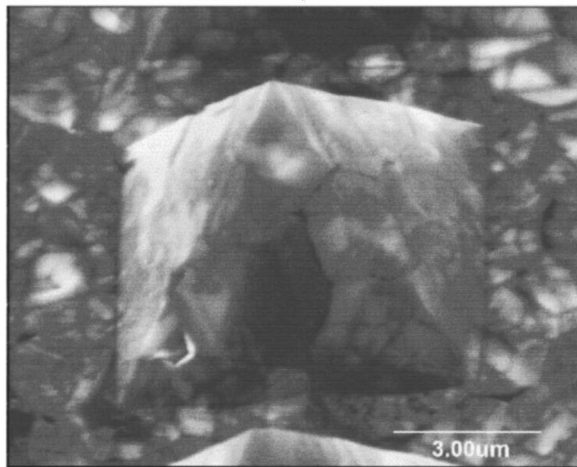
(c)

FIG. 1. Scanning electron micrographs of the emitters fabricated. (a) Type A, CVD diamond film deposited on a flat Si substrate, (b) type B, heteroepitaxial CVD diamond film deposited on a Pt substrate, and (c) type C, pyramidal film fabricated by the transfer mold method.


(a)

(b)

FIG. 2. Measurement system for estimation of the emission field and emission site. (a) Parallel-plate system for general measurements and field determination and (b) point measurement system for site determination.

parallel-plate model is a good approximation, both for H- and for O-terminated samples. The slopes of the Φ curves are 30 and 70 V μm^{-1}, respectively. These values are approximately the same level as the, so to speak, emission field of diamond emitters. However, as shown in Fig. 3(b), the potential curve decreases rapidly just in front of the emitter. This implies that the enhanced electric field is applied to the emitter surface, probably due to the morphology of the film. From this result, it was shown that electric fields of at least 500–1000 V μm^{-1} for H- and O-terminated films are necessary for electron emission. This field is higher than that reported for diamond emitters, 1–100 V μm^{-1}. For the type A emitters with a 10 ppm diborane concentration, similar characteristics were measured. The Φ curve obtained with the type B emitter was also similar to that in Fig. 3, and that of the type C emitters was rounded, similar to that of the etched emitter, but an electric field higher than 500 V μm^{-1} was also necessary. There was no significant difference between the emitters with 1 and 10 ppm diborane concentrations, which agrees with the previous result of less dependence of the emission property on the boron concentration.[6]

C. Measurement of emission site

The emission site distribution was investigated using the point measurement system for type B and C emitters. Figure 4 shows the distribution of $\Phi(d_{EC})$ for type C emitters. The
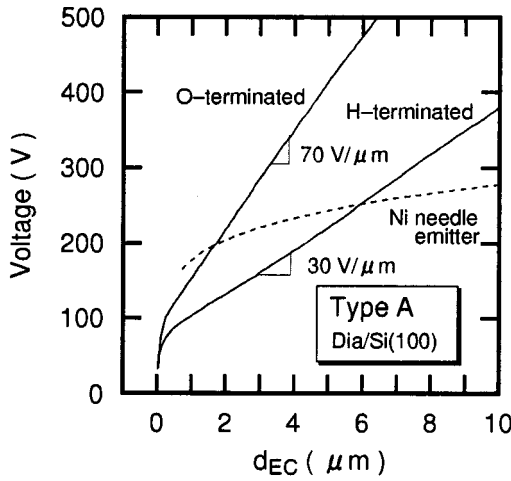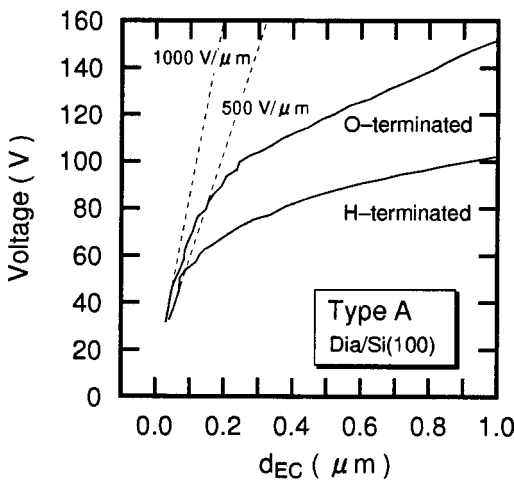
FIG. 3. Relation between the required voltage to extract 0.2 nA emission current and the emitter–collector spacing d_{EC} for the diamond emitter deposited on a flat substrate (type A). (a) Wide range and (b) just in front of the emitter surface. Dashed line in (a) is the relation for a conventional field emitter. Dashed lines in (b) are the tangent lines for Φ curves at the closest point to the emitter.
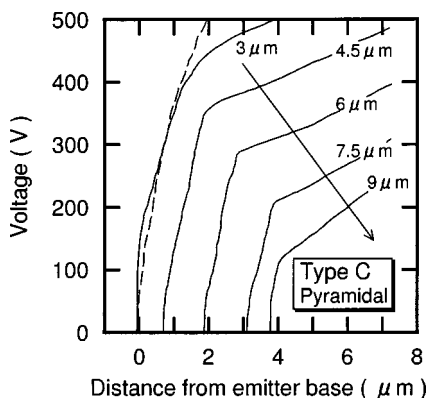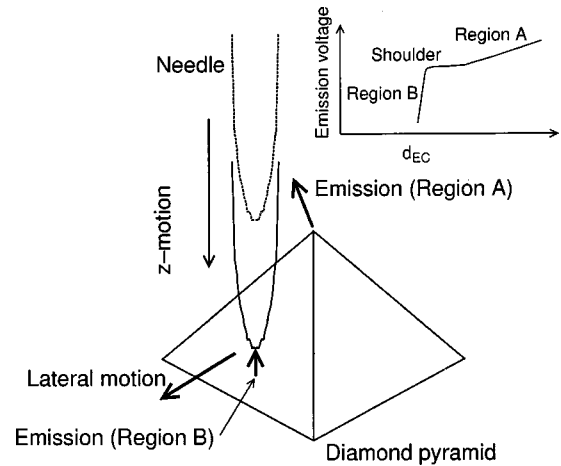

FIG. 5. Schematic of the emission site for the type C emitter with different configurations of the needle and diamond pyramid. The graph in the inset shows a typical relation between voltage and d_{EC}, shown in Fig. 4.

abscissa is the distance from the emitter base (the foot of the pyramid). In Fig. 4, several curves are illustrated and these curves represent the above relationships at different lateral positions. The dashed line shows the characteristics obtained with zero bias for x and y piezos. The curves obtained changed according to the biasing of the x and y piezos along the arrow: at first, the needle approached the emitter base, and then the apex of the pyramid. This clearly shows the present device works as we expected.

In this case, these curves do not represent the potential distribution exactly. Figure 5 is a schematic of the spatial configuration of the needle and diamond pyramid. As is seen in Fig. 4, the curves have a shoulder. The presence of a shoulder in the curve is due to the fact that the needle is off axis with the pyramid. When d_{EC} was large, the electron was emitted from the apex of the pyramid. When the collector is very close to the emitter, there is still some distance, thus large voltage is required for emission from the top of the pyramid. However, if the needle is closer to the base or side face of the pyramid, electron emission will occur suddenly. A rapid fall at close proximity could be explained by the
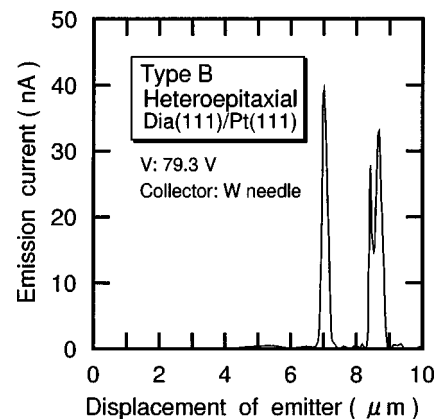

FIG. 4. Relation between the voltage required to extract 0.2 nA and the distance from the emitter base for a type C emitter.

FIG. 6. Relation between the emission current under fixed voltage and the displacement of x and y piezos for a type B emitter.
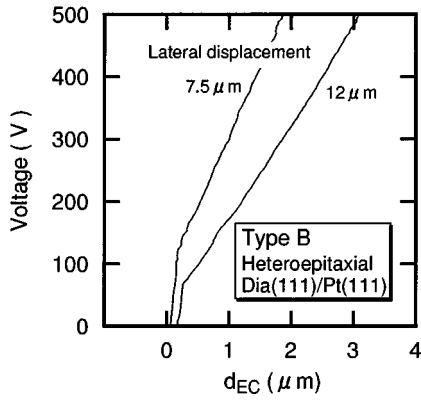
FIG. 7. $\Phi(d_{EC})$ curve at different positions for a type B emitter.

FIG. 8. Schematic of the electric field with different configurations of the needle and crystallite.

present model. Thus, the electron could be emitted even from the flat surface if an adequate field is applied.

Figure 6 shows the emission site distribution of the type B emitter. The abscissa of Fig. 6 is the displacement of x and y piezos (lateral direction) and the ordinate is the emission current. In this measurement, the extraction voltage was kept constant. By biasing the x and y piezos, the emission current varied. It is seen that emission occurred locally. Many runs showed that the current distribution had several peaks but none showed a plateau.

If higher voltage were applied, emission was confirmed at any position. Figure 7 shows the relation between d_{EC} and emission voltage required to extract 0.2 nA at two different positions. For the characteristics at the position of 7.5 μm displacement (position A), the relation is almost linear while for those at 12 μm displacement (position B), a rapid fall just in front of the emitter was seen. From the shape of the curves, the former corresponds to a position above a crystal facet, and the latter corresponds to a position above a crystal edge. Figure 8 shows these two positions, A and B, respectively. It should be noted that the slopes just in front of the emitter were similar to each other. From these results, it is considered that the major emission site is the edge of the crystallites.

IV. DISCUSSION

The present study suggests that the electric field required to emit electrons for boron-doped diamond thin films is at least 500 V μm^{-1}, which is equivalent to 0.5 V nm^{-1}. These values are higher than the reported values, but lower than those for conventional metal field emitters (a few V nm^{-1}). Emission would occur from the edge of the crystallites be-
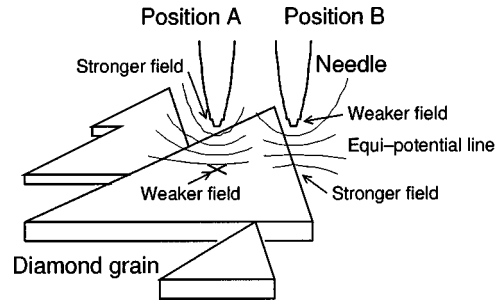
cause of the concentration of the electric field. If this field is applied, it is suggested that, even from a crystal facet, electrons can be emitted. Table II gives a summary of the emission fields and emission sites in the present study. It should be noted that these values are those in front of the emitter, but not exactly at the surface. However, to the authors' knowledge, there is no detailed investigation at this small distance in the literature and the present results may help understanding of the emission mechanism.

Some models have been proposed for the electron emission mechanism from diamond films including p-type diamonds.[17–20] Emission from a negative electron affinity surface[19,20] is not plausible because too high an electric field is required. Some researchers concluded that valence electrons are ejected into vacuum from photoelectron microscopy results.[17] However, for valence electrons, a much higher field would be required. Nevertheless, emission from the valence band cannot be rejected because the present measurements give the minimum field necessary, not the field adequate for emission. Other researchers proposed a model with emission from the subband.[9,21] This is possible from the present results. However, further investigation will be necessary to elucidate the emission mechanism.

V. CONCLUSION

The electric field required for electron emission and the emission site of boron-doped diamond thin-film field emitters was evaluated with measurement systems that can precisely control the position of the collector. The results revealed that the emission field is larger than that reported so far and that the emission site is localized. Localization of the emission site is attributed to the fact that the electric field is enhanced due to the morphology of the diamond films and not to the fact that emission occurs at the grain boundary or

TABLE II. Summary of the emission field and emission site of type A, B, and C emitters.

Term	Type A (typical)	Type B (heteroepitaxial)	Type C (pyramidal)
Emission field	500 V μm^{-1} (H terminated) 1000 V μm^{-1} (O terminated)	>500 V μm^{-1}	500 V μm^{-1}
Emission site	Edge of the grain	Step of the crystallites (crystal facet also)	Apex of the pyramid (side face also)

something like that. If an adequate field is applied, electrons may be emitted from any position on the diamond film. Further investigations will clarify the emission mechanism of diamond thin-film field emitters.

ACKNOWLEDGMENT

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