Development of n-type Diamond Electron Emitter Device

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The authors have developed a high-current electron emitter device using the highly-uniform device fabrication process and phosphorus-doped n-type diamond. Diamond is a highly electron emitting material, and phosphorus-doped n-type diamond has an especially high electron-emission property. The threshold voltage for electron emission from the sharp emitter tip of n-type diamond was lower than that of p-type diamond. Emission properties changed also according to surface conditions. Contrary to the case of p-type diamond electron emitter, in the case of n-type diamond electron emitter, an emitter with an oxygen-terminated surface has a higher emission property than that with a hydrogen-terminated surface. The authors have developed a composite substrate on which n-type diamond can be grown epitaxially to have larger areas than conventional diamond single crystals. This development has consequently led to the successful development of a highly-uniform n-type diamond electron emitter device. Formed at each tip of the diamond emitter, was a nanometer-size coated electrode whose edge was as near as 200 nm from the apex of the emitter tip. The coated electrodes enabled both low-voltage electron emission from n-type diamond and high conductivity of electrodes. By using this n-type diamond electron emitter device, the electron emission current from a 1-mm^2 emission area has reached 1103 mA. The electron emission yield was also as high as 99%. The development of this high-current electron emitter device offers a new approach to many vacuum devices such as microwave transmitter tubes and electron-beam processing machines.

1. Introduction

Diamond is a widely-used industrial material that is attracting much attention due to its excellent physical properties such as high hardness, high Young's modulus and high thermal conductivity. Among the various properties of diamond, negative electron affinity is what enables electrons to be emitted easily from diamond surface. Diamond is therefore highly expected to show good electron emitting characteristics during low-voltage, high-current operations. Sumitomo Electric Industries, Ltd. has been pursuing the development of diamond electron emitter that can be used as a new electron source for applications such as electron beam lithography, microwave tubes and integrated micro vacuum tubes.

The authors had already developed a process for fabricating nano-size diamond tip emitters [(1)] which is a key technology for developing diamond electron emitter devices. A process for fabricating a 3-dimensional gate electrode for each emitter tip was also developed in order to control electron emission current at low voltages [(2)].

Another key technology for providing high current electron source is the application of n-type diamond. For diamond to have electron conductivity, impurities must be doped into it. Compared to p-type diamond whose majority of carriers is holes, n-type diamond whose majority of carriers is electrons is more advantageous for emitting electrons at low voltages.

P-type diamond exists naturally, and it can be easily grown artificially by the high pressure high temperature (HPHT) process or chemical vapor deposition (CVD) process. On the other hand, n-type diamond is difficult to be grown artificially. For example, when nitrogen is doped into diamond, a deep impurity level is exhibited and the doped diamond becomes almost an insulator. In recent years it was found that when phosphorus and sulfur are used as dopants, their doping efficiencies are very low and offer very high resistivity [(3)]. It is reported, however, that n-type diamond synthesized in this manner has high electron emission properties [(4)]. Sumitomo Electric had recently developed a technology for high density doping of phosphorus that allows n-type diamond to have low conductivity even at room temperature [(5)]. Today, n-type diamond is being used as a material for low-voltage, high-current electron emitting sources.

In this report, the authors show that n-type diamond has higher electron emission properties than p-type diamond under various surface conditions. The authors also report on the fabrication of high-current electron emitter device on n-type diamond using the uniform device fabrication technology reported previously.

2. Electron emission properties obtained by different doping and surface conditions

2-1 Electron emission properties of n-type and p-type diamonds

Although it had already been reported that n-type diamond has high electron emission properties [4], [6], measurement had been conducted only on flat epitaxial layer whose emission current is affected by high resistivity at room temperature.

In this report, the heavily doped n-type diamond developed by Sumitomo Electric was used. First, phosphorus-doped n-type diamond and boron-doped p-type diamond were grown on HPHT Ib diamond substrate. The growth conditions are shown in **Table 1**. The phosphorus density in this n-type epitaxial layer is 10^{20} cm^{-3}. The dominant conduction mechanism of this layer is hopping conduction at room temperature and changes to band conduction at temperatures over 100°C. The layer is confirmed to show n-type conduction by the Hall measurement [5]. This heavily doped n-type diamond layer can suppress series resistance at room temperature.

Table 1. Sample growth conditions

	Substrate	Pressure	CH4/H2	Doping gas	Temperature
(A)	Ib(111)	100Torr	0.05%	20%	870°C
(B)	Ib(100)	40Torr	6%	8.3ppm	830°C

Then these samples were dry etched to form tips. A flat anode was positioned at the distance of 100 µm from the tips. This paper is the first report on emitter tip array on n-type diamond. Because the sharp apex of emitter tip creates a large electric field concentration, electrons can be emitted at low voltages. This n-type epitaxial layer is grown on (111) diamond substrate. It is known that work function, which indicates the ability to emit electrons, is different for each crystal plane. Because these diamond samples were fabricated into sharp, needle-like tips, the surfaces of the samples have various crystal planes.

The comparison of electron emission properties of n-type and p-type diamond emitter tips were made in a 10^{-8} Pa vacuum. The current-voltage characteristics are shown in **Fig. 1**. The threshold voltage of n-type diamond was lower than that of p-type diamond. The current-voltage characteristics in **Fig. 1** were converted into a Fowler-Nordheim plot shown in **Fig. 2**. The work function of n-type and p-type diamonds can be calculated from the gradient of the plot. Assuming that both the n-type and p-type diamond samples have the same tip apex radius, the work function of p-type diamond was calculated to be 4.8 eV while that of n-type diamond was 1.4 eV. The work function of n-type diamond is lower than that of conventionally used LaB_6 (2.7 eV), which means that n-type diamond has very high electron emission properties.

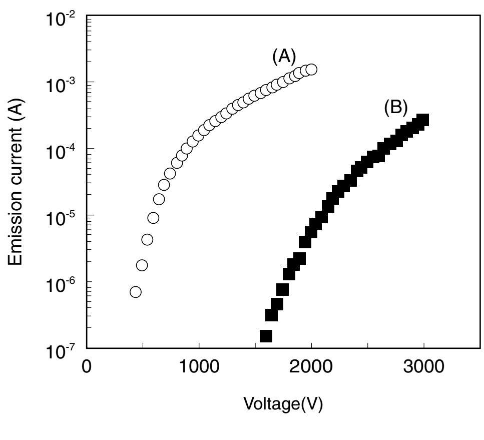

Fig. 1. Electron emission properties of diamond emitter tips
(A) n-type diamond and (B) p-type diamond

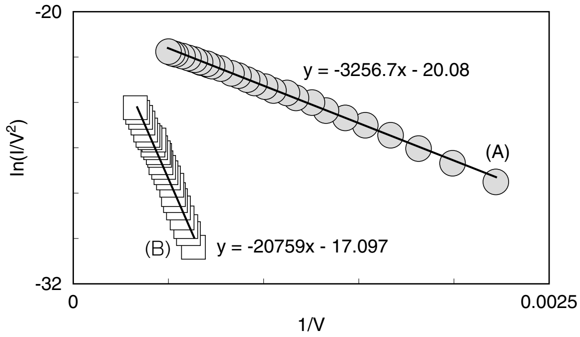

Fig. 2. Fowler-Nordheim plot
(A) n-type diamond and (B) p-type diamond
Work functions calculated from plot gradient: 1.4 eV for n-type diamond and 4.8 eV for p-type diamond.

This can be explained by band diagrams (**Figs. 3(a) and 3(b)**). The vacuum level E_{vac} of p-type diamond having negative electron affinity is just under the conduction band E_c. Because electrons in p-type diamond exist in the valence band that is below the forbidden band, a strong electric field or a high temperature is needed for electrons to overcome vacuum level barrier and emit out of diamond surface. On the other hand, electrons in n-type diamond exist in the conduction band that is above the forbidden band. Although it is known that the conduction band of n-type diamond is bent slightly upward toward the surface [7], the height of vacuum level barrier is much lower in n-type diamond than in p-type diamond. Therefore, weak electric field or low temperature is enough for electrons to emit out of diamond surface.

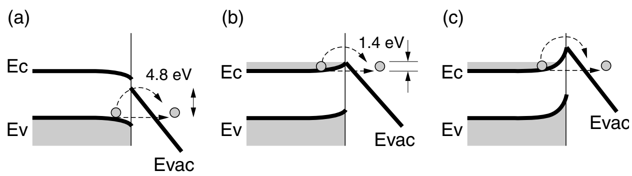

Fig. 3. Band diagrams of diamonds
(a) p-type diamond, (b) oxygen-terminated n-type diamond, and (c) hydrogen-terminated n-type diamond
Electrons are shown to be in gray areas, existing mainly in valence band in p-type diamond, and in conduction band in n-type diamond.

2-2 Electron emission properties obtained by different surface conditions

In order to know the influence of surface conditions on the electron emission properties of diamond, different surface treatments were applied to diamond emitters and their electron emission properties were compared.

When the surface of diamond is exposed to hydrogen plasma, carbon atoms are bonded to hydrogen atoms (hydrogen termination). On the other hand, when diamond is heated in the atmosphere or treated in a strong acid, carbon atoms are bonded to oxygen atoms (oxygen termination). Although the bonding structures vary by surface crystal plane, the bonded atoms significantly change the surface characteristics of diamond.

Surface treatment was applied to the n-type diamond emitters used in Section 2.1. Electron emission properties of both hydrogen-terminated (**Fig. 4(A)**) and oxygen-terminated (**Fig. 4(B)**) diamonds were measured. The distance from diamond emitter to anode was 10 µm. The threshold voltage of oxygen-terminated n-type diamond was lower than that of hydrogen-terminated n-type diamond. This was observed for the first time by the experiment by Sumitomo Electric [(8), (9)]. This tendency is contrary to what was observed in p-type diamond. Because hydrogen-terminated surface produces p-type carriers, hydrogen termination is thought to bend the conduction band upward and increase the barrier height, thus preventing electrons from leaving diamond surface (**Fig. 3(c)**).

These results indicate that oxygen-terminated n-type diamond is the best material for electron emission devices. Starting from the next section, descriptions are given on the process to fabricate devices on this diamond.

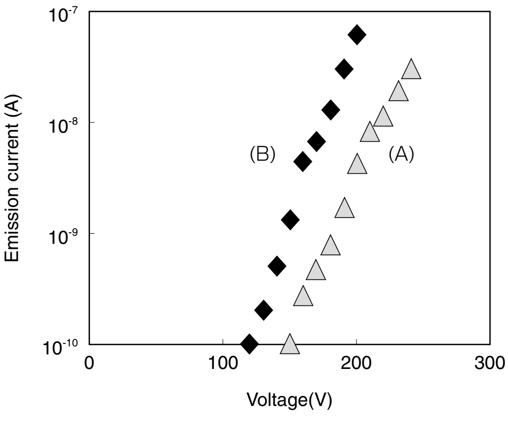

Fig. 4. Electron emission properties of (A) hydrogen terminated and (B) oxygen terminated diamonds

3. Large size n-type diamond substrate

As was previously reported by the authors [(2)], electron emitter device having 3-dimensional gate electrodes can be fabricated more uniformly by using larger sized diamond substrate, because the thickness of photoresist used in the process was highly uniform. Because there is no large difference in conductivity between single-crystal and polycrystal p-type diamonds, polycrystal p-type diamond wafers can be made as large as 2 inches in diameter. However, in the case of n-type phosphorus-doped diamond highly conductive layer can be grown only on (111) plane because doping efficiency is very low on other planes [(5)]. Therefore, if polycrystalline n-type diamond is grown , donor density varies in each grain and only some parts of the device can work. The maximum size available for single crystal diamond having (111) plane is 2.5 mm square through the HPHT process. Recently, the maximum diameter of single crystal diamond having (100) plane grown by the CVD process has reached 10 mm. Because diamond grows defectively in the direction of (111) plane, diamond with (111) plane is still small in size.

When the size of substrate is too small, many processes are subjected to restraints. For example, when photoresist is spin coated on 2-mm single crystal diamond substrate, the thickness of photoresist layer varies by 33% (**Figs. 5(a) and 5(c)**). It is very difficult to fabricate 3-dimensional gate electrodes in high precision on such substrate.

Therefore, the authors have developed 15-mm-square composite diamond wafer that is fabricated by embedding single crystal diamonds by polycrystalline

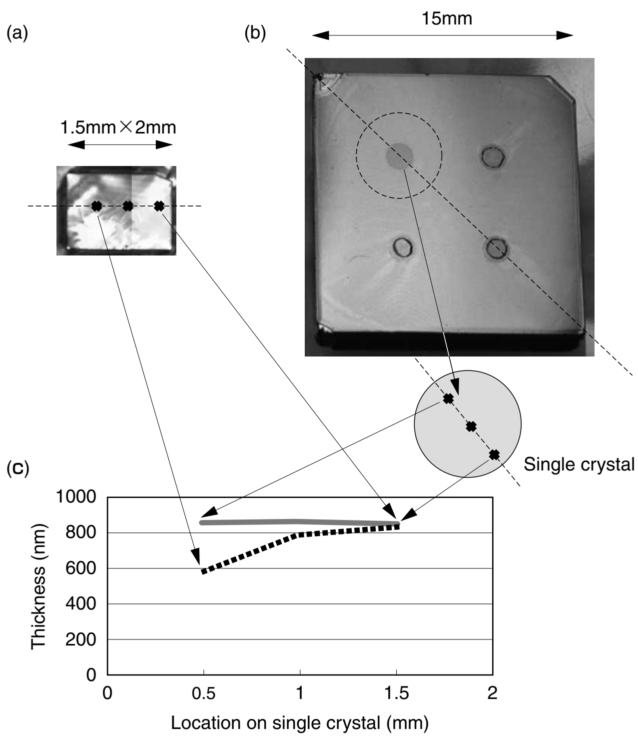

Fig. 5. Photos of photoresist on (a) conventional single crystal diamond and (b) developed composite wafer, and (c) graph showing photoresist thickness variations (33% on single crystal and 1.6% on composite wafer)

diamond growth and then mirror polishing its surface (**Fig. 6**) [10]. On this composite wafer, heavily-doped n-type diamond active layer can be grown on (111) single crystal, and interconnection structure for emission control can be patterned on the surrounding polycrystalline area.

The thickness variation of photoresist on this composite diamond wafer is shown in **Figs. 5(b) and 5(c)**. A uniform thickness was observed and its variation was as small as 1.6%. In the case where electron emitter device was fabricated on conventional small-size single crystal, a half of gate electrodes were not opened by the etching process, because photoresist on one side of the substrate became very thick. Highly uniform gate electrodes were successfully fabricated by using this large composite diamond wafer.

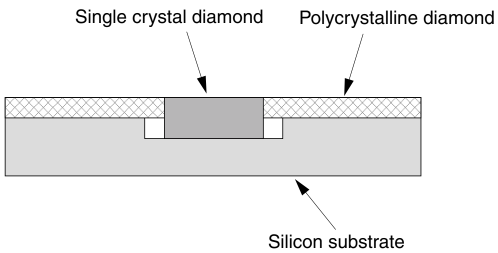

Fig. 6. Cross-sectional image of composite diamond wafer
Single crystal diamond on silicon substrate, fixed by polycrystalline diamond deposition and exposed from mirror polished surface.

4. Electron emitters coated with electrode material

As the fabrication of uniform gate electrodes has become possible, the authors fabricated n-type diamond electron emitter devices and measured electron emission current from emitter to gate electrode (**Fig. 7**). However, the I-V characteristics were different from those in **Fig. 1** . Although the threshold voltage for electron emission of n-type diamond was lower than that of p-type diamond, the rate of rise of emission current of p-type diamond decelerated after exceeding 10^{-5} A, and the maximum emission current of n-type diamond was lower than that of p-type diamond.

To analyze the data, the authors assumed a typical emitter structure as shown in **Fig. 8**, and calculated the DC resistance of this diamond emitter. This emitter structure was approximated by a cylinder with 1 μm diameter and 2 μm high, and because the resistivity of n-type diamond is 600 Ωcm, the resistance per emitter was assumed 15 MΩ Because the diameter of emitter decreases as it nears the tip, the actual resistance becomes even higher than this value. This means that the voltage drop is 150 V when the emission current of a tip is 10 μA. Therefore, resistance cannot be ignored in fabricating large emission current electron sources. On the other hand, p-type diamond can be heavily doped

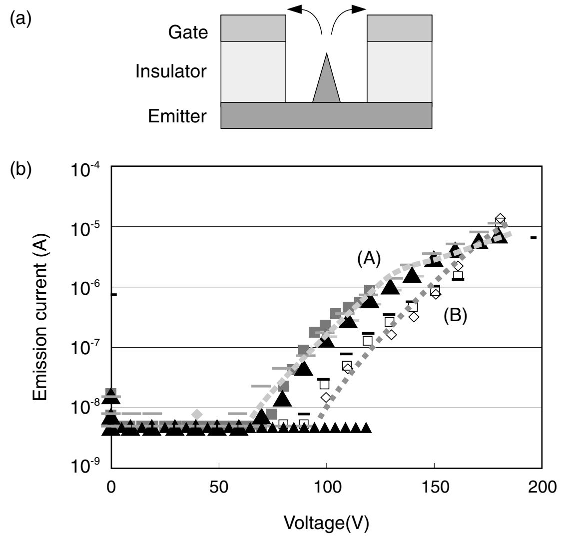

Fig. 7. Electron emission properties of diamond emitter devices
(a) Direction of electron emission in measurement
(b) Electron emission properties of (A) n-type emitter and (B) p-type emitter

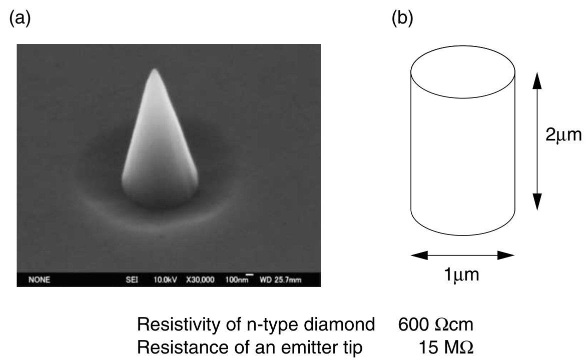

Fig. 8. Emitter tip structure and its series resistance
(a) Structure of emitter tip
(b) Cylindrical approximation model for series resistance calculation (Calculated series resistance per emitter tip: 15 MΩ)

easily and resistance becomes about 4 to 5 orders lower than that of n-type diamond. Therefore, voltage drop can be ignored in the case of p-type diamond.

In order to use the high electron emission properties of n-type diamond and also improve electric conduction, the authors invented a new electron emitter structure. **Figure 9** shows the SEM image of this new diamond electron emitter, which is coated with electrode material but its tip is exposed from the coating. The length between the exposed apex of tip and the edge of electrode coating was less than 200 nm.

After coating electrode material, the self-aligned resist patterning process [2] was applied to this emitter, and SiO_2 insulator and Mo gate electrode were deposited on it. Then photoresist was coated by the self-aligned photoresist process, and opening of gate hole and separation of gate were done by etching. Through this method, 100 electron emission devices each with a 5-μm-pitch tip array were successfully fabricated on a 1 mm^2 area.

the I-V characteristics of the device. When the anode voltage was 2500 V and the gate voltage was 170 V, the anode current and the gate current were 6.7 μA and 17 nA, respectively. The electron emission efficiency was higher than 99%.

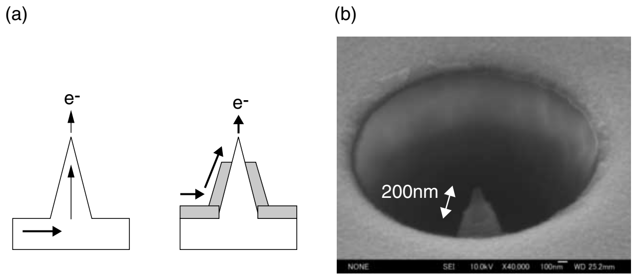

Fig. 9. Emitter tip coated with electrode material
(a) Cross-sectional views of conventional emitter tip and emitter tip coated with electrode material
(b) Emitter tip coated with electrode material and gate electrode

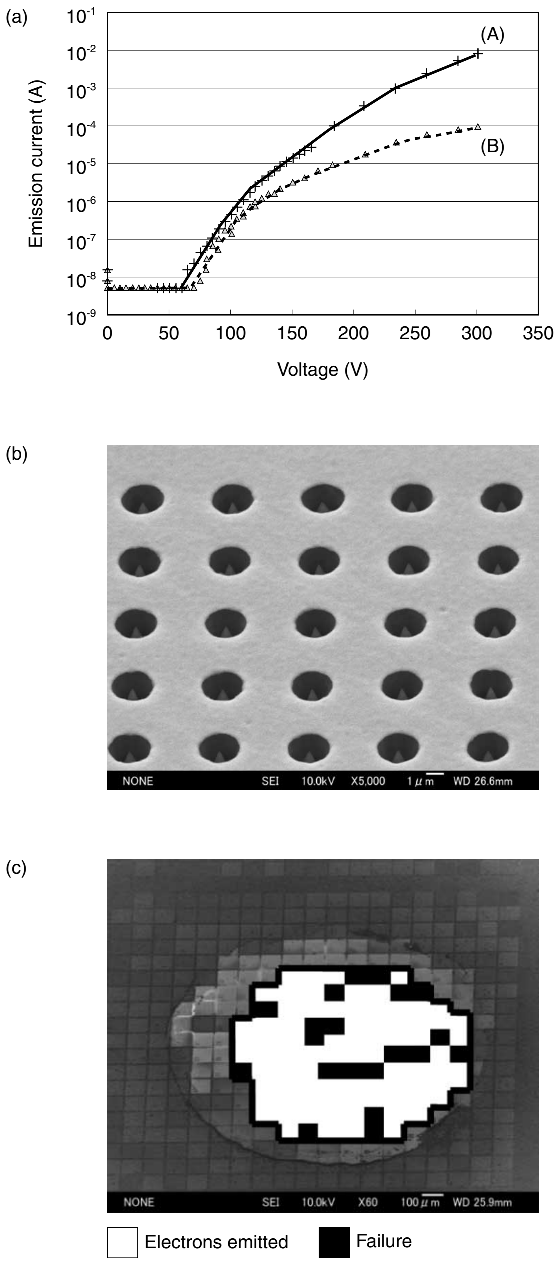

Fig. 10. Electron emission properties of n-type diamond emitter device
(a) Emission properties of devices (A) with electrode material coated on emitter tips and (B) without electrode material coating
(b) Emitter tip arrays with gate electrodes
(c) Device yield in $1mm^2$

5. High electron emission current from n-type diamond emitter device

In a severe environment of high current electron emission, emitted electrons ionize the residual gas on device surface, which causes phenomena such as arc discharge that causes device failures. To avoid this, the authors baked the device at 200°C in vacuum for degassing before conducting measurement. Additionally, the authors conducted the aging process in which pulsed voltage was applied to gate electrode in order to enhance stability of electron emission.

Then electron emission properties were compared between n-type emitter coated with electrode and p-type emitter. The threshold voltage of electron emission of p-type diamond was 100 V. The maximum current from one device at 300 V has reached 14.5 mA. The threshold voltage of electron emission of n-type diamond coated with electrode was 60 V, which was smaller than that of p-type diamond. This is the same value as that of n-type diamond without electrode coating, meaning that coating with electrode did not affect the electron emission properties of n-type diamond. Emission current was always higher than that of p-type diamond, and that from one device at 300 V has reached from several mA to 26.9 mA. By using the process for fabricating uniform devices, the emitter device yield of 100 devices in 1 mm^2 was 82% (**Fig. 10**). Total electron emission current from a 1 mm^2 area reached as high as 1103 mA.

Finally, electron emission efficiency was measured. Anode was placed at 150 μm away from emitter tip. Triode characteristics were measured by applying a voltage to both the gate and the anode of a device. In this case p-type diamond device was used. **Figure 11** shows

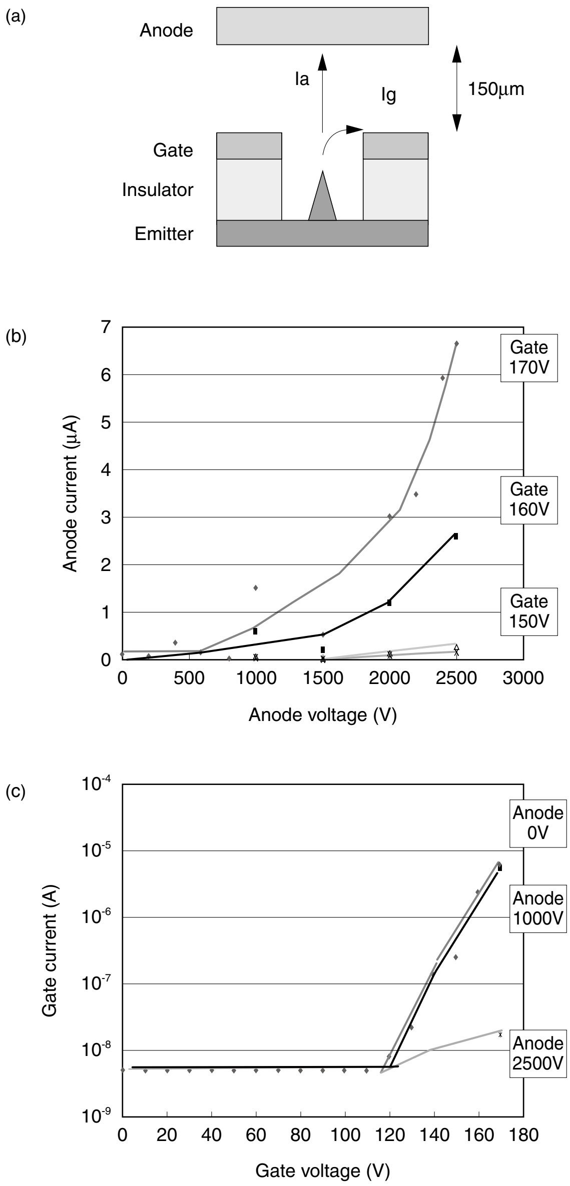

Fig. 11. Triode characteristics of diamond emitter device
(a) Measurement structure of emitter device, (b) anode current measurement result, and (c) gate current measurement result (Electron emission efficiency of 99% at anode voltage 2500 V and gate voltage 170 V)

6. Conclusions

The authors have developed high current electron emitter devices through a process for fabricating highly uniform devices and by using n-type phosphorus-doped diamond whose electron emission properties are especially high among the diamonds. The threshold voltage of electron emission from n-type diamond emitter tips was lower than that of p-type diamond emitter tips. Contrary to p-type diamond emitter, n-type diamond emitter with oxygen terminated surface has higher emission properties than those of emitter with hydrogen terminated surface. The authors have developed a composite substrate on which n-type diamond can be grown epitaxially on larger areas than conventional diamond single crystals, and, consequently, highly uniform devices were successfully fabricated. Electrode material was coated to emitter tips leaving 200 nm from the tip apex uncoated. This electrode coating enables both low voltage electron emission of n-type diamond and high conductivity of electrode. By using this device, the total electron emission current from a 1 mm^2 area has reached 1103 mA. Moreover, electron emission yield was as high as 99%. This high current electron source enables microwave tubes, electr

7. Acknowledgement

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