JVSTB
JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY B

Current-voltage and electron emission characteristics of diamond particles

Guang Yuan, Zhangzhi Gu, Hang Song, and Hidenori Mimura

Citation: J. Vac. Sci. Technol. B **25**, 540 (2007); doi: 10.1116/1.2709900
View online: http://dx.doi.org/10.1116/1.2709900
View Table of Contents: http://avspublications.org/resource/1/JVTBD9/v25/i2
Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Current-voltage and electron emission characteristics of diamond particles

Guang Yuan[a)]
Department of Physics, Ocean University of China, Qingdao 266100, China

Zhangzhi Gu
State Key Laboratory of Surface Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

Hang Song
Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130021, China

Hidenori Mimura
Research Institute of Electronics, Shizuoka University, Hamamatsu, Shizuoka 432-8011 Japan

(Received 17 July 2006; accepted 22 January 2007; published 29 March 2007)

Current-voltage (*I-V*) and electron emission characteristics of two types of diamond particles deposited on Mo tips were measured by using another Mo probe in a scanning electron microscopy chamber. The *I-V* and field emission characteristics of the diamond particles strongly depend on their quality. Ohmic current and no electron emission are observed in a high quality diamond particle, while Pool-Frenkel current and electron emission are observed in a cauliflowerlike particle. Furthermore, to make use of structural and electrical properties of a polycrystalline diamond film, a novel gated diamond cathode with a plane diode structure was fabricated. © *2007 American Vacuum Society.* [DOI: 10.1116/1.2709900]

I. INTRODUCTION

Field electron emission has attracted much attention due to the high potential for variety of electron-beam applications in flat panel displays, high frequency and high power devices, and so on. An essential requirement among these devices is the development of a fine cathode, which produces a stable, high brightness, and uniform electron emission at low driving voltage. Though there are many types of emitters including Spindt-type metal emitters and carbon nanotubes, no emitter has completely satisfied the requirements yet. Diamond related materials including diamond and diamondlike carbon are strong candidates for fine cathode materials because bright field emission has been observed at low electric field.[1–3] The emission mechanism, however, is still under argument.[4–6]

In this article, we deposited two kinds of diamond particles on Mo tips by hot-filament chemical vapor deposition (HFCVD) and measured *I-V* and field emission characteristics by using another Mo probe in a scanning electron microscopy (SEM) chamber. Ohmic current and no electron emission are observed in a high quality diamond particle, while Pool-Frenkel current and electron emission are observed in a cauliflowerlike particle. Furthermore, to make use of structural and electrical properties of the polycrystalline diamond film, which contains insulating diamond and conductive graphite, a novel gated diamond cathode with a plane diode structure was fabricated. Electron emission from the cathode was observed at bias voltage as low as 5 V.

[a)]Electronic mail: yuanguang@ouc.edu.cn

II. EXPERIMENTS

Mo tips were prepared by an anodic oxidation method in a solution of 1 mol/L NaOH and cleaned in de-ionized water and ethanol. Then, without any pretreatment of the Mo tips, diamond particles were deposited by HFCVD method under the following conditions: total pressure of 40 Torr, hydrogen and methane flows of 49 and 1 SCCM (SCCM denotes cubic centimeter per minute at STP), respectively, and Ta filament temperature of about 2000 °C.

Another Mo tip was introduced into a SEM chamber as a measurement probe, and it was fixed to a manipulator so that the probe was adjustable in three dimensions. Mo tips with diamond particles were set on a sample stage of the SEM system and grounded electrically. In other words, a positive bias was applied on the measurement probe, as shown in Fig. 1. After gently adjusting the probe by the manipulator out of the SEM chamber, the contacted region on samples was selected and the *I-V* characteristics were measured. Field electron emission measurements were done after detaching the measurement probe from the diamond particle. The gap between the diamond particle and probe was about 0.1 μm. During the measurement of *I-V* and field emission characteristics, the electron beam in the SEM system was closed to avoid its influence.

In the fabrication of a novel gated diamond cathode with a plane diode structure, thin polycrystalline diamond films were deposited on a silicon wafer with resistivity of 4–5 Ω cm by microwave plasma-enhanced chemical vapor deposition (MWPCVD) technique. After bias pretreatment for enhancing nucleation density of diamond seeds, the diamond deposition was carried out for 1 h to form 0.3 μm thin diamond films under the following conditions; total pressure

 1071-1023/2007/25(2)/540/5/$23.00

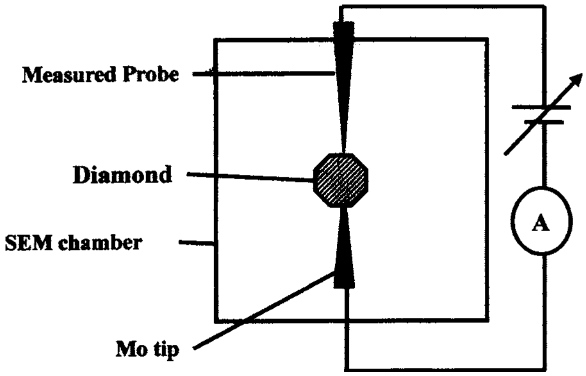


FIG. 1. Schematic of the measurement system of the diamond particles.

of 40 Torr, microwave power of 500 W, and 1% methane in hydrogen. A gold film as thin as 5 nm and 2 mm in diameter was evaporated on the center of the diamond films as an emitting area. Finally a ring gold film with 50 nm thickness and 1 mm width was evaporated at the edge of the thin gold film as a gate electrode in the planar cathode with a diode structure. The field emission from the diamond films with a diode structure was carried out in a high vacuum chamber at 2×10^{-8} Torr, as shown in Fig. 2. A bias voltage lower than 20 V was applied on the gate electrode for the emission measurement and a voltage higher than 100 V was applied on an aluminum anode located at 5 mm away from the cathode to collect the emitted electrons. In the observation of an emission pattern, we replaced the Al anode with a phosphor screen, which was biased at 3.5 kV. The reason for the high voltage such as 3.5 kV is to enhance the brightness of the phosphor screen.

III. RESULTS AND DISCUSSIONS

Figure 3 shows a SEM image and *I-V* characteristic of a high quality diamond particle contacted by a measurement probe. The high quality diamond particle was deposited on a Mo tip for 2 h by HFCVD, and its diameter was bout 6 μm. The particle shows a strong Raman shift peaked only at 1333 cm^{-1}, which means that the particle is a high quality diamond and contains few graphite. The *I-V* characteristic measured in such situation is essentially linear, indicating that the Ohm law rules the current transport in the diamond particle, as shown in Fig. 3. The resistance of the diamond particle is as high as about 2×10^{11} Ω, indicating that the particle is dielectric. Field electron emission measurements were tried after adjusting the measurement probe. However, no field emission was observed.

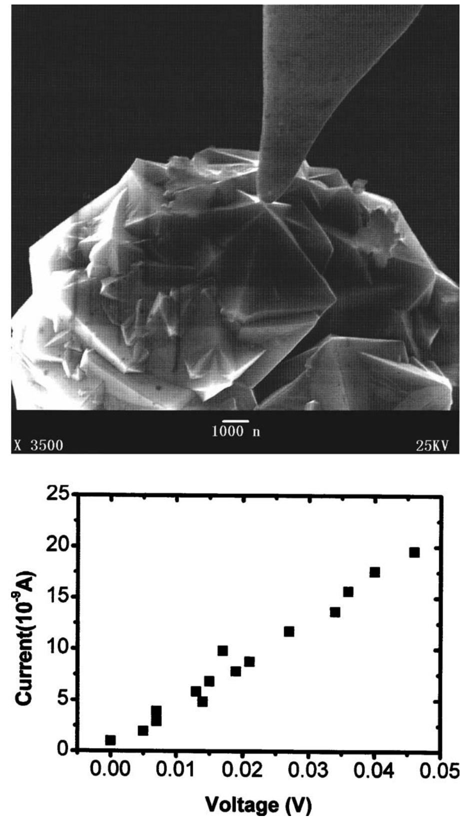


FIG. 3. SEM image of the high quality diamond particle contacted with a measurement probe and its *I-V* characteristic.

Figure 4 shows a SEM image of a cauliflowerlike diamond particle contacted with a dull measurement probe. The diamond particle was deposited on a Mo tip for 40 min by HFCVD in the same conditions as for the diamond particle shown in Fig. 3. Such cauliflowerlike diamond particle is usually conglomerates of many nanocrystalline diamonds and contains a high density of defects and graphite. Because of the rough surface of the particle, special care was paid to select the contact region of the measurement probe. However, the similar *I-V* results were obtained even when the contacted point was changed to other points.

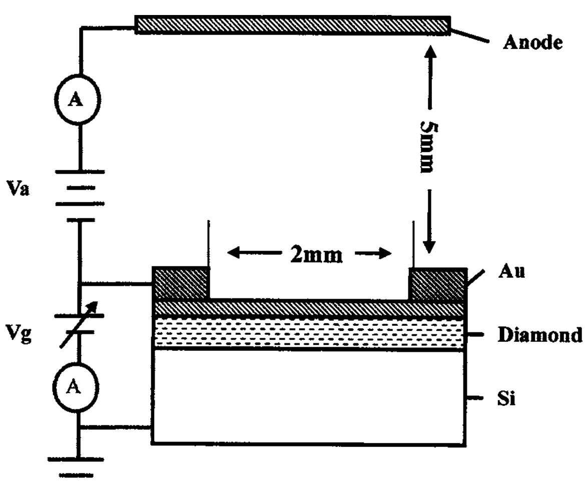


FIG. 2. Schematic of the measurement system of the diamond film with a diode structure.

Figure 5 shows the typical *I-V* characteristic of the cauliflowerlike diamond particle. The *I-V* feature is clearly different from that in Fig. 3. Considering a high density of defects in the cauliflowerlike diamond, "electron hopping" among traps (defects) described by Pool-Frenkel theory is a plausible current transport. The Pool-Frenkel formula is simply expressed as follows:

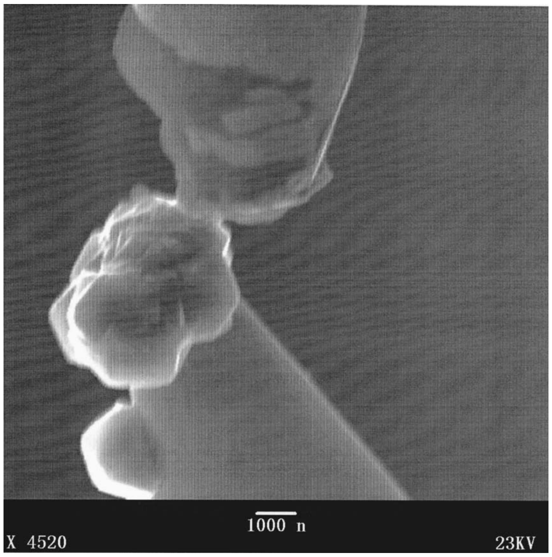


FIG. 4. SEM image of the cauliflowerlike diamond particle contacted with a measurement probe.

$$I=\alpha V \exp(\beta V^{0.5}),$$

where α and β are constants. When we used $\alpha=0.0011$ and $\beta=5.2$, the experimental data agreed well with the Pool-Frenkel theory, except for the bias lower than 0.5 V, as shown in Fig. 5. The β value is related to the permittivity ε of the material and is expressed as follows:

$$\beta=\frac{q\sqrt{q/\pi\varepsilon d}}{kT},$$

where q, d, k, and T are the element charge, space of electrodes, Boltzmann constant, and temperature, respectively. When we used $T=300$ K and $d=1$ μm (particle size), the permittivity ε was calculated to be about 3. This value is smaller than the permittivity of high quality diamond (5.7). The small permittivity of the cauliflowerlike particle is probably due to the high density of defects. Field electron emission was observed from the cauliflowerlike diamond particle. Figure 6(a) shows the dependence of the field emission current on the bias voltage applied on the probe. Figure 6(b) shows the Fowler-Nordheim (F-N) plot.

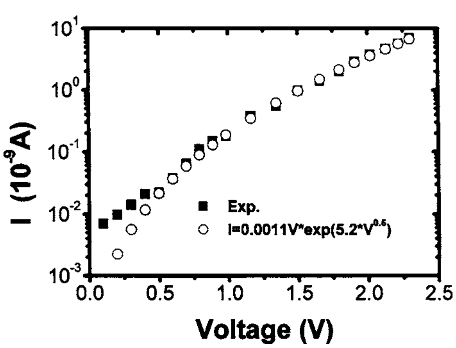


FIG. 5. *I-V* characteristic of the cauliflowerlike diamond particle. Open circles show the calculation by the Pool-Frenkel theory.

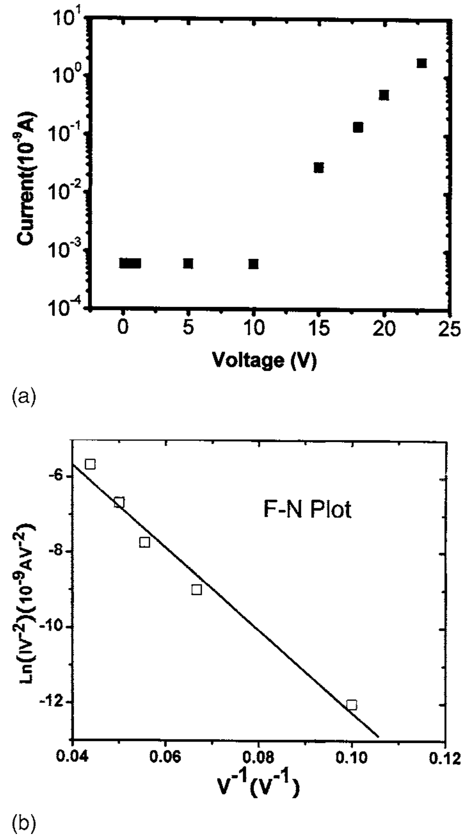
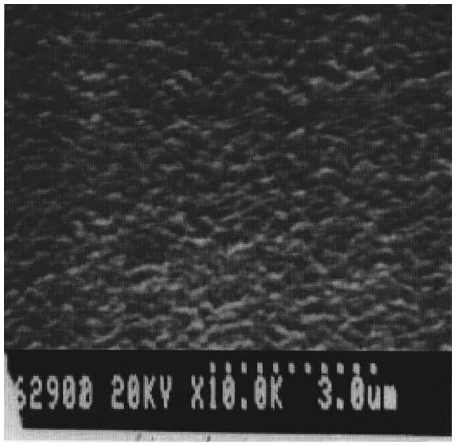


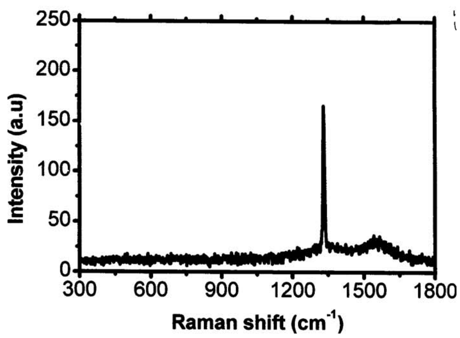
FIG. 6. Field emission characteristic from the cauliflowerlike particle (a) and the corresponding F-N plot (b).

As shown in Figs. 3 and 5, the *I-V* and field emission characteristics of diamond particles depend on their quality. The high quality diamond is essentially dielectric.[7] On the other hand, since the cauliflowerlike diamond contains graphite and defects, which form some energy levels in the band gap of diamond,[8,9] the injection from a substrate to diamond, electron transport in diamond, and field electron emission become possible.

Recently, it was reported that the gated porous Si planar cathode had a low turn-on voltage and uniform electron emission.[10–12] The cathode was simply fabricated by depositing a semitransparent thin Au electrode (about 5–10 nm thick) on oxidized-porous Si formed on a *n*-type Si wafer. That is, the cathode consists of a Au gate electrode, an insulating SiO_2 layer, and a conductive Si nanocrystal. Conventional diamond films deposited by MWPCVD consist of insulating diamond and conductive graphite. Therefore, on the analogy of the gated porous Si cathode, it is expected that the gated diamond cathode, which is fabricated by simply depositing a thin Au gate electrode onto the diamond film, has a low turn-on voltage and uniform electron emission. The SEM image and Raman spectrum of the diamond film used in the gated diamond cathode are shown in Figs. 7(a) and 7(b), respectively. The shift of Raman peaks clearly shows that the film consists of a crystalline diamond phase (a peak at about 1333 cm^{-1}) and a graphite phase (a peak at about 1570 cm^{-1}).

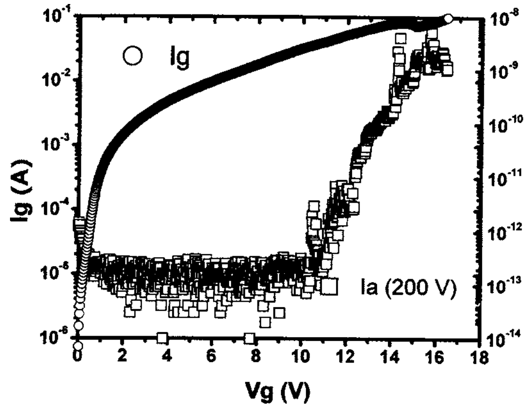


(a)

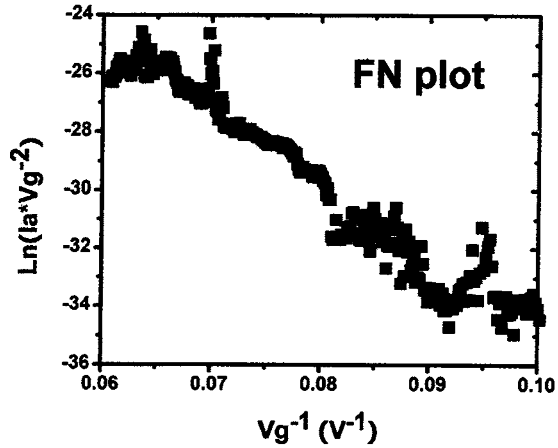


(b)

FIG. 7. SEM images (a) and Raman spectrum (b) of the diamond film used in the gated planar cathode.



(a)



(b)

FIG. 8. Field emission and gate currents from the gated diamond cathode (a) and the corresponding F-N plot (b).

Figure 8(a) shows a typical field emission and a gate current as a function of gate bias. The Fowler-Nordheim (F-N) plot for the emission current gives essentially a straight line, as shown in Fig. 8(b). The field emission was observed at low gate bias as low as 5.3 V, indicating that the gated structure is quite useful for the realization of a low turn-on voltage. At present, the gate current is rather high compared with the emission current. Since the Au gate electrode was deposited onto an as-grown diamond film, the gate electrode was probably in contact with the conductive layer on the top surface of the diamond film. Therefore, the etching of the conductive layer on the surface before the Au deposition could reduce the gate current.

Figure 9 shows the video image of emission pattern observed on a phosphor screen at the gate voltage of 15 V. The horizontal stripes observed in the emission pattern are scanning lines of a TV monitor. The size of the image was about 4 mm in diameter, which was about twice of the emitting area formed by the thin gold film. The scattering angle of the emitted electrons is smaller than 6°, suggesting that electrons are emitted from the plane cathode with little angular dispersion.

IV. CONCLUSIONS

The *I-V* and field emission characteristics of two types of diamond particles were measured by introducing a measurement probe into a SEM chamber. The current transport of the cauliflowerlike diamond particle is ruled by the Pool-Frenkel mechanism, while Ohmic current is the dominant process for the high quality diamond. The field emission is observed from the cauliflowerlike particle, but the high quality diamond shows hardly emissive. Furthermore, to make use of structural and electrical properties of a polycrystalline diamond film, which contains insulating diamond and conductive graphite, a gated diamond cathode with a plane diode

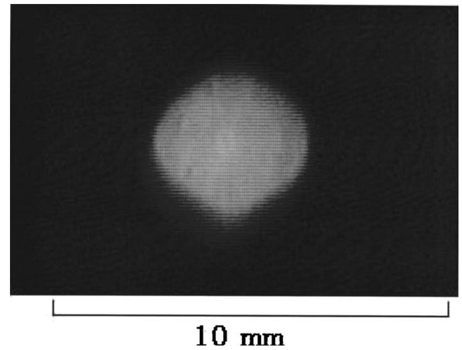


FIG. 9. Emission pattern of the gated diamond cathode observed on a phosphor screen.

structure was fabricated. The cathode shows a low turn-on voltage of 5.3 V and uniform electron emission.

ACKNOWLEDGMENTS

The authors would like to thank C. Kimura, H. Tamai, T. Sato, and M. Arai of New Japan Radio Co. Ltd. for fruitful discussions and M. Unno of the Institute of Multidisciplinary Research for Advanced Materials, Tohoku University for Raman experiments. The authors are also deeply indebted to H. Shimawaki and K. Sagaya for their help in the deposition of diamond.

[1]K. Okano, S. Koizumi, and J. Ito, Jpn. J. Appl. Phys., Part 2 **34**, L1068 (1995).
[2]K. Okano, S. Koizumi, S. Silva, and G. Amaratunga, Nature (London) **381**, 140 (1996).
[3]M. W. Geis, N. N. Efremow, K. E. Krohn, I. C. Twichell, T. M. Lyszczarz, R. Kalishi, J. A. Greer, and M. D. Tabat, Nature (London) **393**, 431 (1998).
[4]F. Himpsel, J. Knapp, J. VanVechten, and D. Eastman, Phys. Rev. B **20**, 624 (1979).
[5]J. Robertson, J. Vac. Sci. Technol. B **17**, 659 (1999).
[6]N. S. Xu, Jun Chen, and S. Z. Deng, Appl. Phys. Lett. **76**, 2463 (2000).
[7]H. Mimura, G. Yuan, M. Ikeda, and K. Yokoo, Jpn. J. Appl. Phys., Part 1 **42**, 4048 (2003).
[8]Y. Muto, T. Sugino, K. Kobashi, and J. Shirafuji, Jpn. J. Appl. Phys., Part 2 **31**, L4 (1992).
[9]T. Sugino, Y. Muto, K. Karasutani, J. Shirafuji, and K. Kobashi, Diamond Relat. Mater. **2**, 803 (1993).
[10]N. Koshida, T. Ozaki, X. Sheng, and H. Koyama, Jpn. J. Appl. Phys., Part 2 **34**, L705 (1995).
[11]T. Komoda, X. Sheng, and N. Koshida, J. Vac. Sci. Technol. B **17**, 1076 (1999).
[12]H. Mimura, K. Miyajima, and K. Yokoo, J. Vac. Sci. Technol. B **21**, 1612 (2003).