Effect of Surface Treatment on Field Emission Properties of CVD Diamond

Hideki KAWAMURA, Tetsuro MAKI and Takeshi KOBAYASHI

Graduate school of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan Phone/Fax: +81-6-850-6313/6341, E-mail: kawamura@sup.ee.es.osaka-u.ac.jp

1. Introduction

Diamond is a promising material for a high efficiency electron emission devices due to its negative electron affinity (NEA).^(1,2) As far, several electron emitters which have quite low turn-on field has reported.⁽³⁾ Also, diamond electron emitters have a great advantage in the stability of the emitted current because of its hardness, high thermal conductivity and chemical inertness. However, it is a serious problem that the properties of the diamond surface change a lot with its adsorbed atoms.^(4,5,6,7) Electron emitters suffer ion bombardment all the time, so the control of the diamond surface is necessary to stabilize the electron emission. In this study, we investigated the emission properties of the hydrogenated, oxidized and fluorinated surfaces of polycrystalline diamond films and discussed the mechanism of the electron emission.

2. Experimental

All samples are undoped polycrystalline diamond films grown by electron-cyclotron-resonance (ECR) microwave plasma-assisted chemical vapor deposition (CVD) using H₂/CO (222/12 sccm) gaseous source. Substrates are scratched *p*-Si (100) wafers and the thickness of diamond films are 1-2 μ m. Figure 1(a) and (b) show the SEM micrographs of the surface morphology and the cross



Fig. 1 (a) SEM image of the typical diamond surface. (b) SEM image of the cross section of the diamond film. (c) Schematic structure of the electron-emission measurement system.

section of the typical sample, respectively. It is well known that the as-deposited surface has the surface conductive layer and this surface is terminated by hydrogen atoms.⁽⁸⁾ As-deposited (H-terminated) diamond films were divided into several pieces. Some pieces were annealed in oxygen atmosphere (500 °C, 0.3 Torr) to obtain the oxygen terminated surface.⁽⁹⁾ The surfaces of other pieces were fluorinated by the electron beam evaporation of CaF₂ film at 500 °C.^(10,11) The measurement of the emission properties from the fluorinated surface was performed after the removal of CaF₂ films by hydrochloric acid.

Figure 1(c) shows the measurement system of the field emission current. Samples were mounted in a vacuum system with a pressure of $\sim 1 \times 10^{-6}$ Torr.

3. Results and Discussion

Figure 2 shows the electron emission properties of the as-grown (H-terminated) surface obtained at several anode to diamond spacings. The turn-on field stood at 6-7 $V/\mu m$ for any cases. We can say the obtained current above the turn-on field was due to the tunneling effect because it could be described well by the modified Fowler-Nordheim law,

$$J = F \frac{1.54 \times 10^2 (\beta E)^2}{\phi} \exp\left(\frac{-6.83 \times 10^3 \phi^{3/2}}{\beta E}\right), \qquad (1)$$

where J is the current density in A/cm², F the fraction of the area emitting electrons, E the field in V/ μ m, ϕ the work function in eV, and β the factor of the geometrical field enhancement mainly controlled by the cathode radius of curvature. The electric field E was calculated simply as E = V/d, where V is the anode-cathode voltage and d is the spacing between the anode and the cathode. If we assume $\beta = 1$, the work function is estimated to be very low around 0.06 eV.

The field enhancement must be caused due to the surface asperity, but the value of $\beta = 500-800$ estimated from $\phi = 4-5$ eV seems much larger than we imagine from Figs. 1(a) and (b). As many authors reported that the diamond films of high graphite or defect content exhibit superior properties as an electron emitter, we also consider the some kinds of defects induce the additional energy states within the band gap and contribute to the electron emission. That is, electrons are transported through these states and finally emitted from the surface states a little below conduction band minimum.



cathode spacings. (a)I-E characteristics; (b)F-N plot.

The electron emission properties of H-, O- and Fterminated surfaces are shown in Fig 3. It was confirmed by SEM that the surface morphology was not affected by several surface treatment. According to the another experiment using a homoepitaxial CVD diamond film, it is also confirmed by LEED observation that the deposition and the removal of CaF₂ film do not disorder the crystallinity of the surface. Then, we can assume the factor β has same value in each surface. Suppose $\beta = 1$, the work functions of H-, O- and F- terminated surface are estimated to be $\phi_H =$ 0.06 eV, $\phi_O = 0.09$ eV and $\phi_F = 0.08$ eV, respectively.

It is natural that the surface states are centered at various levels depending on the foreign adsorption atoms, and the result obtained from Fig. 3 reflects it. We found the relationship of the work function between H-, O- and Fterminated surfaces, $\phi_H < \phi_F < \phi_O$. The energy levels from which electrons are emitted are centered closer to the conduction band on the H-terminated surface than on the Oterminated surface. As for the fluorinated surface, Yun *et al.* reported that residual oxygen in the vacuum chamber might be adsorbed to this surface during fluorination by CaF₂ deposition at the elevated temperature.⁽¹²⁾ Then, we may say the work function of the fluorinated surface is smaller than that of the oxidized surface, but we cannot conclude that the work function of the fluorinated surface is higher than that of hydrogenated surface. By the way, it is likely that



Fig. 3 Electron emission properties of the Hterminated, O-terminated and F-terminated diamond surfaces. (a)I-E characteristics; (b)F-N plot.

fluorinated surface has an advantage in the stability of the emitted current because fluorination of diamond surface can reduce the surface energy,⁽¹³⁾ so that more elaborate work will be needed to investigate the potential of the fluorinated surface as an electron emitter.

4. Conclusions

We investigated the field emission properties of polycrystalline diamond thin films grown by ECR microwave plasma CVD. These surfaces are terminated with hydrogen (as-grown), oxygen (annealing in O_2 ambient) and fluorine (CaF₂ deposition at elevated temperature). The work function of these surfaces obtained from the slope of F-N plot was quite low. Both the field enhancement due to surface roughness and the electronic states centered in band gap might contribute to the electron emission. The work function estimated here clearly depended on several surface treatments.

References

- F. J. Himpsel, J. A. Knapp, J. A. Van Vechten and D. E. Eastman: Phys. Rev. B 20 (1979) 625
- M. W. Geis, J. A. Gregory and B. B. Pate: IEEE Trans. Electron Devices 38 (1991) 619
- K. Okano, T. Yamada, H Ishihara, S. Koizumi and J. Itoh: Appl. Phys. Lett. 70 (1997) 2201
- 4) M. I. Landstrass and K. V. Lavi: Appl. Phys. Lett. 55 (1989) 975
- T. Maki, S. Shikama, M. Komori, Y. Sakaguchi, K. Sakuta and T. Kobayashi: Jpn. J. Appl. Phys. 31 (1992) 1446
- 6) B. B. Pate, M. H. Hecht, C. Binns, I. Lindau and W. E. Spicer: J. Vac. Sci. Technol. 21 (1982) 364
- 7) N. Eimori, Y. Mori, A. Hatta, T. Ito and A. Hiraki: Jpn. J. Appl. Phys. 33 (1994) 6312
- 8) Y. Mori, N. Eimori, J. S. Ma, A. Hatta, T. Ito and A. Hiraki: Appl. Surf. Sci. 56 (1992) 89
- 9) Y. Mori, N. Eimori, A. Hatta, T. Ito and A. Hiraki: Jpn. J. Appl. Phys. 31 (1992) L1718
- 10) S. Suzuki, Y. Otsuka, T. Maki and T. Kobayashi: Jpn. J. Appl. Phys. 35 (1996) L1031
- T. Ando, J. Tanaka, M. Ishii, M. Kamo, Y. Sato, N. Ohashi and S. Shimosaki: J. Chem. Soc. Faraday Trans. 89 (1993) 3105
- 12) Y. Yun, T. Maki and T. Kobayashi: J. Appl. Phys. 82 (1997) 3422
- 13) S. Miyake: Appl. Phys. Lett. 65 (1994) 1109