Temperature dependence of surface band bending and field emission for boron-doped diamond and diamond-like films

Sheng-Yuan Chen and Juh-Tzeng Lue

1 Department of Electrical Engineering, National Tsing Hua University, 30042, Taiwan, Republic of China
2 Department of Physics, National Tsing Hua University, 30042, Taiwan, Republic of China
E-mail: jtlue@nthu.edu.tw

New Journal of Physics 4 (2002) 79.1–79.7 (http://www.njp.org/)
Received 20 June 2002, in final form 2 October 2002
Published 24 October 2002

Abstract. In this experiment we have measured the temperature dependence of field emission characteristics for boron-doped diamond and diamond-like films at various temperatures and low fields. The threshold voltage increases and emission current density decreases as the temperature decreases. These field emission characteristics can be successfully explained by the semiconductor thermionic emission theory. This measurement apparently reveals that the electron affinity is not changed while bending down of the surface band is enhanced as temperature decreases, resulting in reduction of the emission current.

Recently chemical vapour deposited (CVD) diamond films have become a prominent material for field emission display devices due to their excellent thermal and chemical properties, especially the prevalence of negative electron affinity (NEA) [1]–[3]. Much effort has been devoted to field emission studies of NEA in CVD diamond films at rather high temperatures and low electric fields [4]–[6].

In many studies [6]–[8] the Fowler–Nordheim (FN) equation [9] has been implemented to model the results of field emission of diamond films and to calculate the work function. However, the FN equation is derived for electron field emission from normal metal surfaces at high fields and low temperatures, and the temperature effect can be easily demonstrated by adjusting the work function to fit the data [12]. There have been some improved theoretical models [13]–[15] for studying the field emission of diamond films. Further, some experimental results have

† Author to whom any correspondence should be addressed.
been reported [16]–[18] which illustrate the temperature dependence of the field emission of phosphorus-doped diamond films. But, there are few published studies of the temperature dependence of field emission for boron-doped diamond films using theoretical models.

We have developed [19] a theoretical model for solving the field emission of a semiconductor, the results of which conclusively fit our experimental data on the temperature dependence of field emission for boron-doped diamond and diamond-like films.

Polycrystalline boron-doped diamond films were grown on a p-type (100)-oriented Si substrate by an Astex 5400 microwave plasma enhanced chemical vapour deposition (MPECVD) system. The detailed procedure has been described in previous reports [19, 20]. To study the effect of temperature on the field emission, the samples were mounted on the cooling stage of a helium closed-cycle refrigerator. The diamond film was separated from the anode (indium–tin oxide coated glass) by a 50 µm Teflon spacer. Typical measurements were made as the sample cooled down from room temperature to 20 K. A programmable current source provided a step-wise constant current with output voltages varying from 0 to 1100 V.

On account of the low electron affinity, electrons emitted from a p-type semiconductor are presumed to comply with the emission current of metal–insulator–semiconductor (MIS) Schottky barrier diodes [21], with the total emission current density being given by

\[ J_{\text{total}} = J_c + J_v + J_s \]  \hspace{1cm} (1)

where \( J_c, J_v \) and \( J_s \) are the emission current densities, which are proportional to the tunnelling probability from the conduction band, the valence band and surface states respectively. Bandis and Pate [22] alluded that field emission from surface states is unlikely, implying the negligibility of \( J_s \). A tedious manipulation of equation (1) can yield a simple formalism [19] given by

\[ J_{\text{total}} = a_1 T^2 e^{-\theta/kT} e^{-b_1 \chi^{3/2}/F} + a_2 \frac{1}{\chi + E_g} F^2 e^{-b_2 (\chi + E_g)^{3/2}/F} \]  \hspace{1cm} (2)

where

\[ a_1 = \frac{q m k^2}{2 \pi^2 \hbar^3}, \quad b_1 = \frac{4 \sqrt{2} m}{3 q \hbar} v(y), \quad a_2 = \frac{q^2 m}{16 \pi^2 m \hbar^2 t^2(y)}, \quad b_2 = \frac{4 \sqrt{2} m}{3 q \hbar} v(y), \]

\( v(y) \) is a tabulated function involving elliptic integrals, \( \chi \) is the electron affinity, \( t(y) \) is another tabulated function, \( \theta \) is the difference energy between the surface conduction band minimum and the Fermi level and \( F \) is the external electric field.

To study the effect of temperature on the field emission, the samples were measured in cycles of cooling down and warming up. The plots of dependence of current density on electric field at various temperatures are depicted in figure 1. The curves illustrate that the currents decrease and the turn-on voltages increase as temperature decreases. For example, the turn-on voltage is about 7 V µm\(^{-1}\) at 300 K. At this temperature, the current density increases to 40 µA cm\(^{-2}\) at a field of 22 V µm\(^{-1}\). Apparently, at 20 K, the turn-on voltage increases to 10 V µm\(^{-1}\), and the current density decreases to 10 µA cm\(^{-2}\) at the same applied voltage. This tendency is similar to our previous study of boron-doped diamond-like films [23]. The decrease in emission current may be due to the increase in the surface barrier as the temperature decreases. In that work we used the FN equation to express the temperature dependence of the emission current by tacitly assuming the increase in work function as temperature decreases. Other groups [10, 11, 17, 18] have claimed that field emission characteristics are independent of temperature for boron-doped diamond films. The different conclusions reached in those works were made using data measured from room temperature up to 350 or 200 °C not as in our case measured from room temperature...
Figure 1. The temperature dependence of field emission for boron-doped diamond films. The symbols are experimental data and curves are theoretical fittings with parameters as given by $a_1 = 1.12 \times 10^6 \text{ A m}^{-2} \text{ K}^{-2}$; $b_1 = 1.02 \times 10^{38} \text{ kg}^{-1/2} \text{ m}^{-2} \text{ A}^{-1}$; $a_2 = 1.56 \times 10^{-10} \text{ A}^3 \text{ s}^4 \text{ kg}^{-1} \text{ m}^{-2}$; $b_2 = 1.02 \times 10^{38} \text{ kg}^{-1/2} \text{ m}^{-2} \text{ A}^{-1}$; $E_g = 5.5 \text{ eV}$, $v(y) = 0.95$, $t(y) = 1$. The thermionic emission of semiconducting films essentially reveals a non-zero but negligible current for all voltages, especially when the spacer thickness is too thin to introduce a leakage current whereupon the threshold voltage is determined as the current becomes appreciable.

down to 20 K. Secondly, in [10] and [11], the emission current measured at 10 V $\mu$m$^{-1}$ showed no difference between 250 and 300 K, unlike the present data. The thinner spacer thickness (50 $\mu$m) used in this experiment in comapred with those used in [17] and [18] (125 $\mu$m) implies a larger enhancement factor.

Figure 2 shows the temperature variation of the electron affinity $\chi$ and the energy difference between the surface conduction band and the Fermi energy $E_{cs} - E_f$ derived from the theoretical fitting of figure 1. The band bending of the surface conduction band $E_{cs} - E_f$ increases as the temperature decreases, while the electron affinity $\chi$ is almost independent of temperature. The latter result testifies to the fact that the occupied surface density of states is reflected in the surface chemical adsorption [24, 25]. More electrons flow out from the surface states into the valence band leaving more positive ions at the interface as the temperature decreases. The bending down of the conduction band at the surface will be more pronounced at low temperatures.

Previously [23], we tacitly assumed that the drop in emission current was attributable to the increase in the surface barrier height as the temperature decreased, as predicted by the

New Journal of Physics 4 (2002) 79.1–79.7 (http://www.njp.org/)
Figure 2. The theoretical fitting for boron-doped diamond films with $\chi$ the electron affinity; $E_{cs} - E_f$ is the energy difference between the surface conduction level and the bulk Fermi level.

FN equation. But the FN equation, which contains only one parameter of the material, the effective surface barrier $\phi_s$, is insufficient to describe the band diagram of diamond. Apparently a monotonic experimental curve can be readily fitted by any exponential or power-law function by merely adjusting one variable, and the FN equation has been ubiquitously used with published data by changing the work function to fit the results for various temperatures. However, the simulated work functions derived in [23] are too small to reveal the real physical values. In the thermionic equation, we include two fundamental parameters, the electron affinity $\chi$ and the surface band bending energy, $E_{cs} - E_f$. Thereby we can clearly elucidate the band diagram as shown in figure 3 for the field emission process. It clearly illustrates electron tunnelling through the surface barrier. In cases where there is a density of states due to the absorption of gases, with a Fermi level higher than that of the bulk of p-type diamond film, the flow of electrons causes band bending near the surface. The Fermi level of surface states depends on the detailed, temperature-dependent properties of the chemical bond of the adsorbed molecular species. As the temperature increases, fewer electrons flow from surface states to the p-type diamond bulk, resulting in the bending down of the surface band becoming shallow. The increase in the turn-on voltage is due to the increased band bending as the temperature is decreased. We have not observed the NEA for large-scale non-single-crystalline diamond films. The negative $\chi$ can only be detected at some special orientations of the crystal and at hydrogenated surfaces.
Figure 3. Schematic energy band diagrams for (a) high temperature; and (b) low temperatures, respectively.

Figure 4. The temperature dependence of field emission for boron-doped diamond-like films.

The bending down of the surface conduction band at lower temperatures results in a lower value for the electron emission. Similar results for boron-doped diamond-like films are shown in figures 4 and 5. The electron affinity retains its original value at various temperatures. The work function for diamond-like films has a larger value than that for diamond films, resulting in a lower electron emission current at the same applied bias.

This work shows that the field emission current comes predominantly from the conduction band for p-type diamond and diamond-like films and is very dependent on temperature. The conventional FN equation is not suitable for treating the emission current at low fields and non-
Figure 5. Theoretical fitting for boron-doped diamond-like films with $\chi$ the electron affinity and $E_{cs} - E_f$ the energy difference between the surface conduction level and the Fermi level.

zero temperatures. The behaviour of the field emission characteristics can be well expressed by a similar theory for the thermionic emission current of MIS Schottky barrier diodes. The empirical fitting results show that the electron affinity is unaffected while the bending down of the conduction band increases as temperature decreases.

Acknowledgments

This work was supported by the National Science Council of the Republic of China under contract NSC 91-2112-M007-057 and the Ministry of Education under contract 91-FA-04-AA.

References

[1] Himpsel F J, Knap J A, van Vechten J A and Eastman D E 1979 Phys. Rev. B 20 624
[2] van der Weide J and Nemanich R J 1994 Phys. Rev. B 49 13629
[3] Robertson J 1996 Diamond Relat. Mater. 5 797
[4] Xu N S, Latham R V and Tzeng Y 1993 Electron. Lett. 29 1595
[5] Okano K, Yamada T, Ishihara H, Koizumi S and Itoh J 1997 Appl. Phys. Lett. 70 2201
[6] Bunshah R F, Jou S and Doerr H J 1996 Thin Solid Films 280 256
[7] Bozeman S P, Baumann P K, Ward B L, Powers M J, Cuomo J J, Nemanich R J and Dreifus D L 1996 Diamond Relat. Mater. 5 802
[8] Okano K and Gleason K K 1995 Electron. Lett. 35 74
[9] Fowler R H and Nordheim L W 1928 Proc. R. Soc. A 119 173

New Journal of Physics 4 (2002) 79.1–79.7 (/http://www.njp.org/)
[10] Glesener J W and Morrish A A 1996 Thin Solid Films 290–291 153
[11] Glesener J W and Morrish A A 1996 Appl. Phys. Lett. 69 785
[12] Gomer R 1961 Field Emission and Field Ionization (Cambridge, MA: Harvard University Press) p 19
[13] Huang Z H, Cutler P H, Miskovsky N M and Sullivan T E 1994 Appl. Phys. Lett. 65 2562
[14] Jensen K L 1995 J. Vac. Sci. Technol. B 13 516
[15] Forbes R G 1999 J. Vac. Sci. Technol. B 17 526
[16] Kimura C, Kuriyama K, Koizumi S, Kamo M and Sugino T 1999 Appl. Surf. Sci. 146 295
[17] Sugino T, Kuriyama K, Kimura C, Yokota Y, Kawasaki S and Shirafuji J 1999 J. Appl. Phys. 86 4635
[18] Sugino T, Kuriyama K, Kimura C and Kawasaki S 1998 Appl. Phys. Lett. 73 268
[19] Chen C L, Chen C S and Lue J T 2000 Solid State Electron. 44 1733
[20] Chen C S, Chen C L and Lue J T 2000 Eur. Phys. J., Appl. Phys. 11 3
[21] Lue J T 1980 Solid State Electron. 23 263
[22] Bandis C and Paté B B 1995 Phys. Rev. B 52 12056
[23] Lue J T, Chen S Y, Chen C L and Lin M C 2000 J. Non-Cryst. Solids 265 230
[24] Ristein T 2000 Diamond Relat. Mater. 9 1129
[25] Rutter M J and Robertson J 1998 Phys. Rev. B 57 9241