Field emission properties of ta-C films with nitrogen doping

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We have studied the electron emission characteristics of tetrahedral amorphous carbon (ta-C) films with different nitrogen content. With increasing N content in ta-C, the room-temperature conductivity as well as the emission current decreases and then increases, resulting in minima. The Fermi level shifts toward the conduction band and, thus, the work function decreases by N doping in ta-C, however, the emission currents of doped ta-C films are less than those of undoped ta-C.
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I. INTRODUCTION

Recently, the field-emission display (FED) has attracted much attention as one of the most promising flat panel displays because of its similarity to the cathode ray tube (CRT). It is thin and light weight even though its display quality is similar to that of the CRT. A typical field-emission display uses microfabricated cold cathode tips made of metal or crystalline silicon.[1,2] The display uses a huge number of fine microtip cold cathodes as the electron sources. However, these materials have high work function, leading to high driving voltage. One of the methods to decrease the driving voltage is to employ low work function material such as diamond or diamondlike carbon (DLC) as the cathode tip material. The tetrahedral amorphous carbon (ta-C) has a high sp^3 fraction and, thus, is considered as a promising material for efficient electron emission. The filtered cathodic arc is widely used to deposit ta-C among several deposition methods.

The ta-C contains no hydrogen and has the remarkable properties of high density and high hardness similar to diamond.[3–5] The films are smooth and can be deposited at low temperature, making them potentially useful for electronic applications. When considering the possible use of ta-C as a cold cathode material, the control of the Fermi energy through the band gap by doping should be done to reduce its work function. The work function is considered to be related to the turn-on field for electron emission. It has been shown that successful n-type doping of ta-C by phosphorus incorporation is possible without changing its tetrahedral structure.[6] Phosphorus is a shallow donor in ta-C even though its large size compared with the C atom, but its solubility is too low in order to act as a donor. Meanwhile, nitrogen, a deep donor in diamond, occupies a substitutional site distorted along the (111) direction.[7]

In this work, we studied the electron emission properties of nitrogen-doped ta-C films. We have employed two kinds of doping methods; *in situ* doping with control of N_2 partial pressure in the cathodic discharge and ion-shower doping on the grown ta-C films. The emission currents and the threshold field for field emission depend strongly on N content in ta-C.

II. EXPERIMENT

The ta-C films were grown by filtered cathodic vacuum arc plasma with various acceleration voltages.[8] The nitrogen was doped by two methods; *in situ* gas-phase doping in the arc plasma and ion-shower doping on grown ta-C. The partial pressure of N_2 was varied to control the N content.[9] On the other hand, the acceleration voltage, ion current, and ion-doping time are the main parameters for ion-shower doping.[10] The nitrogen ions were doped by a fixed acceleration voltage of 6 kV, with N_2 pressure of 30 mTorr and ion flux of 3.4×10^{13}/s. The temperature dependence of conductivity for the 90 nm thick ta-C film was measured with an electric field of 1000 V/cm in which the linear current–voltage relationship has been satisfied. The electron emission

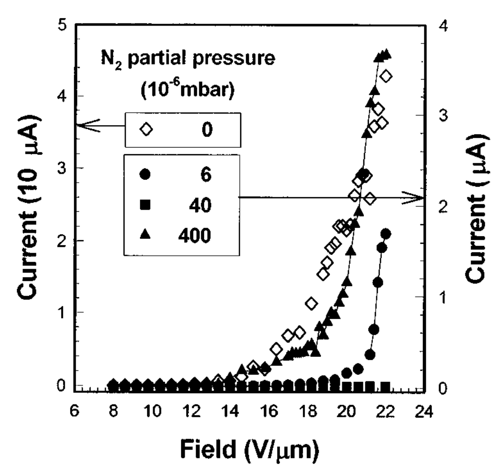

FIG. 1. The current–electric field (I–E) characteristics of gas-phase nitrogen-doped ta-C films.

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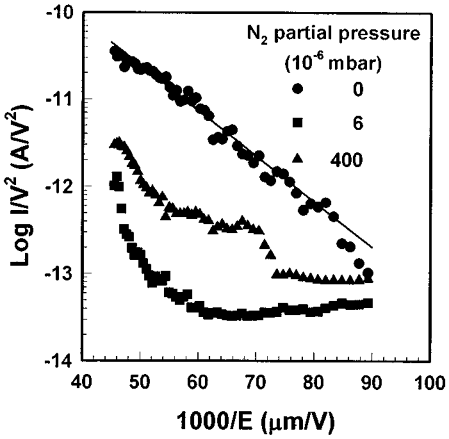

FIG. 2. The Fowler–Nordheim (FN) plots of gas-phase nitrogen-doped ta-C films.

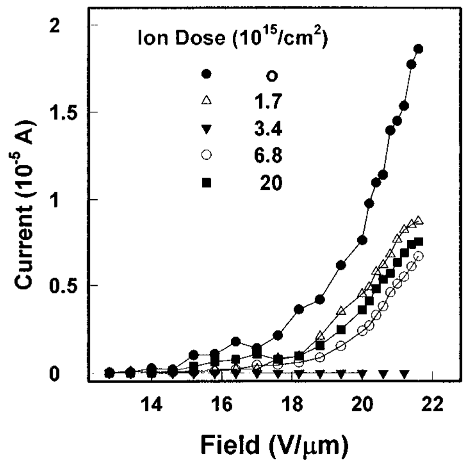

FIG. 4. The $I-E$ characteristics of N-doped ta-C films with various ion doses.

currents were measured in a vacuum of 1×10^{-7} Torr, between the metal and DLC plates, with an area of 0.9 cm^2 and 50 μm spacing.

III. RESULTS AND DISCUSSION

Figure 1 shows the current (I)–electric field (E) characteristics of the gas-phase N-doped ta-C films. The nitrogen partial pressure was changed from 0 to 4×10^{-4} mbar. The emission current decreases with increasing nitrogen partial pressure up to 4×10^{-5} mbar, and then increases with nitrogen partial pressure.

Figure 2 shows the Fowler–Nordheim (FN) plot of the emission currents for the ta-C films. Undoped ta-C film follows FN tunneling in wide field range. Meanwhile, the currents from doped ta-C films seem to deviate from the FN plot, especially in the low-field region.

The ta-C film was doped by an ion shower of N_2 plasma. The film was deposited by using filtered cathodic arc deposition (FAD) with a 90 V substrate bias. Figure 3 shows the room-temperature conductivity of the N-doped ta-C film. The conductivity decreases with increasing ion dose up to 6.8×10^{14} cm^{-2} and then it increases with the ion dose. The decrease of the conductivity is related to the shift of the Fermi level toward the midgap.

Another sample was deposited by using FAD with a 200 V substrate bias. The deposited ta-C on a low resistant Si wafer was ion doped for emission current measurements. Figure 4 shows the $I-E$ characteristics of ion-doped ta-C films with various ion doses. The emission current decreases with increasing ion dose up to 1.7×10^{15} cm^{-2} and then increases with an ion dose similar trend to conductivity. Figure 5 shows the Fowler–Nordheim lots of the emission currents for undoped and heavily N-doped ta-C films. The emission currents satisfy FN tunneling.

Figure 6 shows conductivity and emission current of ion-doped ta-C films versus ion dose. The emission current was

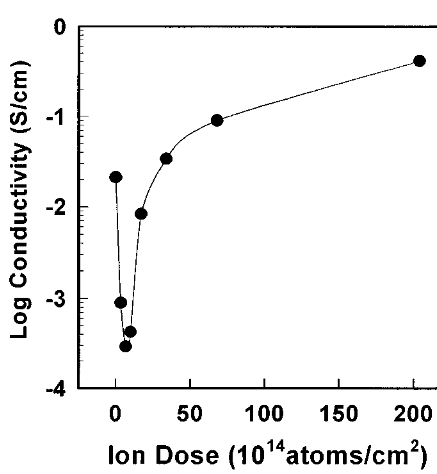

FIG. 3. The room-temperature conductivity of N-doped ta-C film vs ion dose.

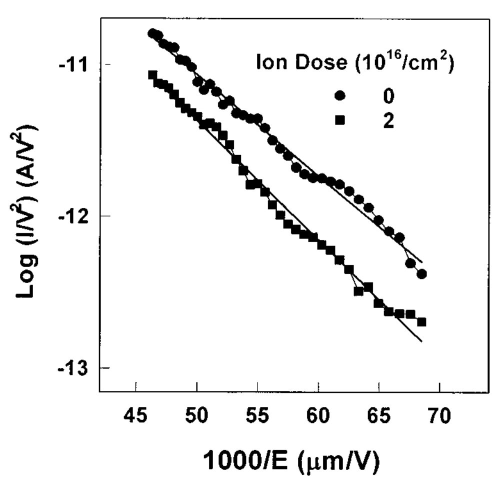

FIG. 5. The comparison of FN plots between undoped ta-C and heavily N ion-doped ta-C.

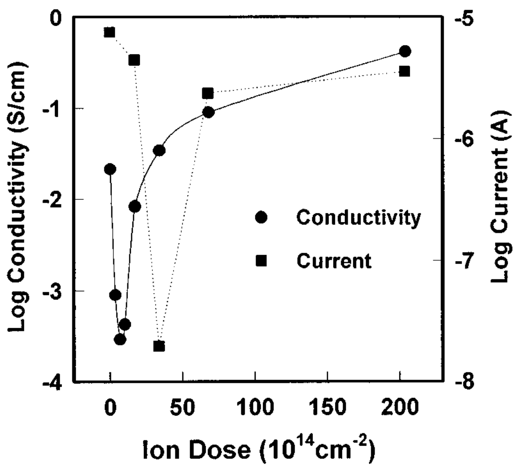

FIG. 6. Ion-doping effect on the conductivity and emission currents for the ta-C films.

measured at 20 V/μm. The emission current and room-temperature conductivity have a similar trend, but have minimums at different ion dose.

Two kinds of N doping in ta-C have been carried out in our study and we obtained the same trend in emission currents as well as in room-temperature conductivity, the emission current and the conductivity decrease with N content up to a certain level and then it increases. It is noted that undoped ta-C shows p-type conduction, but it becomes n-type material by N doping, whether the doping method is gas phase or ion shower. It is interesting that n-type doping can be possible in ta-C by the ion-doping method because it is believed that effective n-type doping is impossible in diamond.

The emission currents for the doped films are less than those of undoped ta-C showing p-type conduction. This is quite a contrast to the fact that plasma-enhanced chemical vapor deposition DLC has a higher emission current after a high dose ion doping than undoped DLC.[11]

From the above experimental observations, we can draw a conclusion that the emission current from ta-C is not enhanced even though its work function is lowered by N doping. The electron emission mechanism is not clear now, so that more studies should be carried out in order to clarify it.

IV. CONCLUSION

The effect of nitrogen doping on the electron emission characteristics for ta-C films was studied by using gas-phase and ion-shower doping methods. With increasing N content in ta-C, the room-temperature conductivity as well as emission current, decrease and then increase even though the conductivity and emission minimums occur at different N content. The emission current of n-type ta-C is less than that of undoped ta-C, leading to a conclusion that the electron emission from ta-C does not increase with decreasing its work function by n-type doping.

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