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Electron Emitter of Negative Electron Affinity Diamond

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A new type of electron emitter device of chemical-vapor-deposited diamond thin film is proposed. The device is a diode of metal-insulator-semiconductor (MIS) structure consisting of an intrinsic polycrystalline diamond film as the insulator, an aluminium electrode on one side, and hydrogenated diamond surface on the other side as the p-type semconductor with negative electron affinity (NEA). Electrons will be injected and/or excited to the conduction band of intrinsic diamond layer to be emitted from the hydrogenated diamond surface of NEA.

Key words : Diamond, Negative Electron Affinity, Electron Emitter, Thin Film

I. Introduction

Negative electron affinity (NEA) of diamond surface[1] is expected to realize a stable and efficient cold cathode for microvacuum electronics devices[2,3] and multi emitter display panels. Many efforts have been devoted to understand and control the interesting features of diamond surface.[1-11] By using the NEA diamond surface, a high efficiency is expected in electron emission because the electrons excited to the conduction band can freely go down to the vacuum level below the conduction band minimum. Such the electron emission from the NEA surface will depend mainly on the electron affinity itself rather than morphological factor which affects the extracting field for field emission. An efficient emissivity over large area of a flat NEA surface will perform stable electron emission and will realize long-life-time cold cathode whereas the field emitter degrades due to concentration of emission current to the focus of extracting filed.

M.W. Geis fabricated a diamond cold canode of p-n junction for the first time in which electrons are injected to B-doped p-type semiconducting diamond from "n-type like" layer created by ion implantation with heavy dose.[12] The current density was estimated as 0.1-1.0 A cm^{-2} and the cathode efficiency, as a ratio of emission current to the diode current, was varied between 2×10^{-6} and 1×10^{-10}. One should pay attention to that the emission was enhanced after introducing oxygen into the vacuum system. G.R. Brandes fabricated a similar junction device replacing the implanted layer with P-doped homoepitaxial diamond as "n-type".[13] The emission current was in the order of fA because of poor conductivity in the P-doped diamond. In this paper, we investigate a cold cathode of MIS structure, in which electrons are injected from the metal through a schottky junction or can be avalanched in the intrinsic layer at high electric field.

The diamond surface has been studied by photoemission spectroscopy, electron energy loss spectroscopy, ion beam analysis, TEM observation, and so on. It was confirmed that the hydrogenated diamond surface had NEA while oxidized one shows positive electron affinity. The electron affinity can be controlled to be negative or positive by hydrogenation or oxygenation, respectively, in plasmas or anneal in hydrogen or oxygen. It was found that vacuum ultra violet light could convert the positive electron affinity into negative one by replacing the oxygen with hydrogen, which would be one of the key techniques to fabricate the diamond-based electronics devices. It has become possible to pattern the localized NEA areas in a diamond surface.

We should pay attention to the fact that the hydrogenated diamond surface for NEA also has p-type conductivity though its mechanism has not been understood yet.[14,15] If the diamond was covered with such the conductive layer, it would be made difficult to apply electric field to the junction or diamond bulk which is necessary for injection, acceleration or excitation of electrons. The conductive layer of hydrogenated diamond surface can be easily removed by oxidation. For the electron emitter device, however, such the surface conductive layer of p-type can be used instead of B-doped diamond. The hydrogenated surface of diamond will perform not only the NEA feature for the emission but also p-type layer for the MIS structure. In designing a diamond cold cathode, the diamond surface should be oxidized for insulating while leaving partly hydrogenated area for emission.

The design and fabrication procedure of the NEA diamond emitter is described in the following section. The performance of electron emission from the emitter is measured and discussed.

II. Experimental Procedure

Figure 1 is the cross sectional drawing of the cold

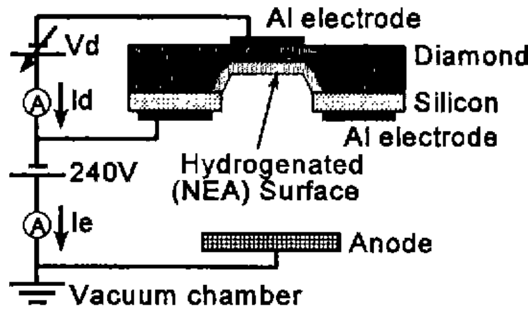

Fig. 1. Cross sectional drawing of the NEA diamond electron emitter by MIS structure. Electrons are injected into diamond from the Al electrode.

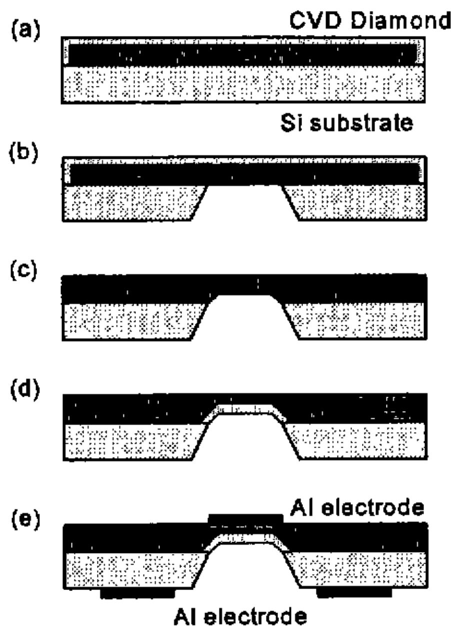

Fig. 2. Fabrication procedure of the NEA diamond emitter device. (a) Un-doped diamond film is fabricated on silicon substrate by the microwave plasma CVD. The as deposited diamond surface has the conductive layer. (b) A small hole, 2 mm in diameter, is made by etching in HF. (c) The diamond film is thinned from the back side by ECR plasma etching with oxygen gas. The surface conductive layer is completely removed by following anneal in oxygen at 500°C. (d) The back side surface of the thinned diamond film is hydrogenated by irradiation to hydrogen ECR plasma at low temperature with leaving the top side surface still resistive. (e) Al electrodes are deposited by an electron beam evaporator.

cathode of diamond thin film. Electrons are injected into intrinsic diamond by the MIS structure of Al/ intrinsic diamond/hydrogenated diamond surface (p-type semiconducting). The electrons are injected through the schottky junction and accelerated in the intrinsic layer to be emitted from the hydrogenated surface without substantial escape from the conduction band. The intrinsic layer should be thinned enough to allow the electrons to reach the surface. The avalanched electrons will be also expected at a high electric field in the intrinsic layer which would remarkably enhance the emission current.

Table 1. Growth Condition of the Diamond Film for the Emitter by the Microwave Plasma CVD

Reaction Gas	CO (10 sccm)/H2 (90 sccm)
Reaction Pressure	4 kPa
Microwave Power	250 W
Substrate Temperature	950°C
Deposition Time	12 hr

Table 2. Etching Condition of the Diamond film for the Fabrication of Thin Diamond Layer

Reaction Gas	O_2 (100 sccm)
Reaction Pressure	1.33 Pa
Microwave Power	600 W
Substrate Temperature	280°C
Substrate Bias	-30 V
Etching Time	1 hr

The upper surface of the diamond film should be oxidized to isolate between the Al electrode and Si substrate. The fabrication procedure of the cold cathode is described in detail in the following section and the performance of the emitter is evaluated in the results.

The fabrication procedure of the cold cathode is shown in Fig. 2 A polycrystalline diamond film of about 10 μm thick was deposited by conventional microwave plasma CVD on a 500 μm-thick p-type silicon (100) substrate under usual condition listed in Table 1. A hole of about 2 mm in diameter was etched out in the silicon substrate from the backside. The diamond film was thinned from the backside by oxygen ECR plasma etching for 1.5 hr under the condition of Table 2. The etching rate of the CVD diamond by the oxygen plasma was estimated in another experiment as 0.1 μm/min. The resulting thickness of the diamond film was expected to be about 1 μm. However, the thickness was not always uniform because of roughness of both the as-grown and asetched surfaces. It has been known that the as grown diamond surface was covered with the conductive layer. The conductive layer was removed by the following anneal in oxygen at 500°C. After the oxidation, only the backside surface was hydrogenated again by irradiation to hydrogen ECR plasma at 280°C while leaving the upper side still resistive. The device was completed by deposition of Al electrodes by vacuum evaporation after removal of silicon oxide by HF dipping, one of which was for the MIS structure on diamond and the other of which was for the ohmic contact to the silicon substrate.

III. Results and Discussion

Figure 3 shows and I-V characteristic curve of the MIS

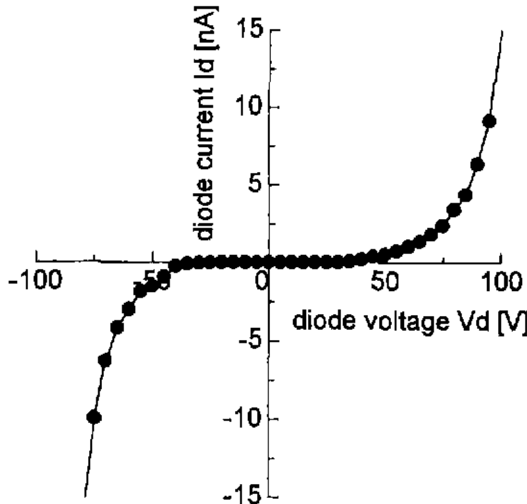

Fig. 3. Diode current versus the diode voltage.

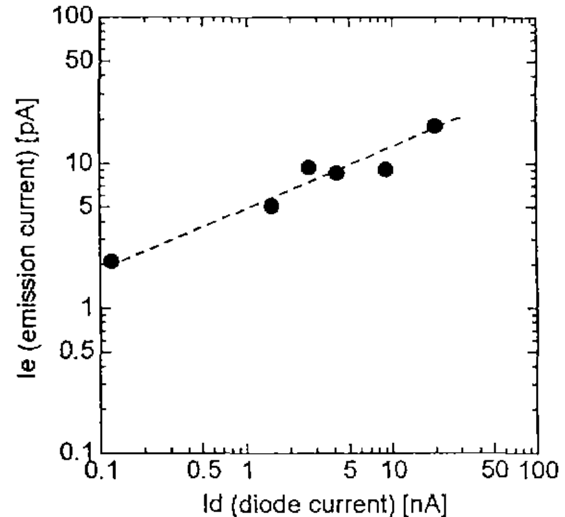

Fig. 4. Emission current versus the diode current.

diode. The diode current rapidly increased from 30 V in forward biasing while it broke down at 40 V in backward biasing. Because of imperfectness in the diamond film deposited, such as boundary and roughness, the measured current would include some leakage current through some different paths from the MIS structure. Supposing that the break down voltage of -40 V was fully applied to the 1-μm thick diamond film, the break down field of the film was estimated as 4×10^5 Vcm^{-1}. it was more than one order smaller than the value of single crystalline diamond, 3.5×10^6 Vcm^{-1}.[16]

The electron emission from the cold cathode was investigated in an ultra-high vacuum chamber at 10^{-7} Pa using the experimental circuit schematically shown in Fig. 1. The whole circuit for diode current, electrically floated from the grounded vacuum chamber, was positively biased as to be+240 V at the emitter surface with respect to the chamber. The total emission current for the biasing. An grounded anode was located at about 1 cm from the emitter surface only for correction of emission current. The extracting field due to the bias voltage of 240 V was still too small to extract electrons by itself

The electron emission appeared after the rapid increase in the diode current when the applying voltage for the diode exceeded 40 V. The emission current increased with increasing the diode current Figure 4 shows the emission current versus the diode current. The maximum of the emission current was 20 pA at the diode current of 15 nA when the diode voltage was 100 V, which was the maximum of the power supply used in the present study for the diode current. The efficiency of electron emission as a ratio of the emission current to the diode current was nearly 2% at maximum. With increasing the emission current, however, it decreased to 0.1% at 20 pA emission. The deterioration in the cathode efficiency would be due to increase in leakage current of small contribution to the electron emission. To improve the performance of the electron emitter, it is necessary to increase actual diode current through the MIS structure, i.e., electron injection into the intrinsic diamond where also the avalanche current will be expected at high electric filed. Improvement in uniformity in film quality and film thickness of the intrinsic layer would realze a NEA cold cathode with high efficiency and large emission current.

IV. Summary

A cold cathode of thin diamond film was designed for electron emission from the NEA diamond surface, and was fabricated by microwave plasma CVD and ECR plasma etching. The emitter consisted of MIS structure for injection and acceleration of electrons and a hydrogenated diamond surface of NEA. The cold cathode worked at a low threshold voltage of 40 V for electron emission and a high cathode efficiency of 2% though the current was still small (2pA). The performance of the cathode will be improved by more precise fabrication, such as uniformity in thinning and control of crystal boundary in the film.

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