

Electron Field Emission from Carbon Films after Dielectric Breakdown and the Activation Process

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The activation process of the electron field emission characteristics from poly-crystalline diamond films has been studied. Poly-crystalline diamond films locally emit the electrons in the extracting electric field. The emission property is enhanced by applying a high electric field for the activation. By the activation, enhancement of emission property from original emission sites and production of new emission sites were confirmed. The structural change of the film by the activation was in the scale out of observation by scanning electron microscope (SEM).

Key words: diamond, electron field emission, activation

1. INTRODUCTION

It is promising to use the carbon material such as chemical vapor deposited (CVD) diamond films, diamond like carbon (DLC) films and carbon nanotubes (CNT) for the cold cathode of field emission display (FED). Diamond had been expected to emit electrons efficiently due to the negative electron affinity (NEA). It has been evident that the surface of the type IIb natural diamond has the characteristics of NEA[1]. It was also found that the poly-crystalline diamond films emitted electrons at a low electric field[2]. In the latter report, however, it was shown that the spatial distribution of the photoelectron emission was different from that of the field electron emission. It was inferred that the electron field emission was not always caused by the characteristics of NEA but originated from the poor quality of the diamond films. It has been confirmed that the diamond films of rather poor quality emit electrons easily[3-5]. It has been also found that the electron field emission from diamond films is not from the faces but from the localized specific point, so called "emission site". It is supposed that some microstructures in the diamond films, such as boundaries, non-diamond phases, or inclusions, can be the emission sites.

It has been known that the electron field emission from poly-crystalline diamond films is greatly enhanced by the pretreatment, so called, "activation" or "initiation". The emission sites are activated or initiated by applying a high electric field to the films. It is argued that the activation of the emission sites occurs through the dielectric breakdown of insulating material resulting in conductive microstructures in the insulating bulk.

In this study, electron field emission from undoped diamond films is enhanced by applying a high voltage on the films, and the activation of emission sites is investigated.

2. EXPERIMENTAL DETAILS

The electron field emission properties of poly-crystalline

diamond films were measured before and after the activation process of applying a high voltage.

The poly-crystalline diamond films were grown on n-type silicon (100) substrates for 12 μ m thick by an ASTeX AX6300 plasma deposition system with a CH₄/H₂ ratio of 3/97 which was higher than the usual ratio of 1/99. The fabricated diamond films at the high CH₄ concentration were rather poor in quality while they emitted electrons easily. The deposition process was terminated by hydrogen plasma treatment for a few minutes to induce the surface conductive layer on the diamond film.

Figure 1 shows the experimental set up used for the electron field emission measurements. Measurements were performed in a ultra high vacuum chamber evacuated to better than 10⁻⁷ Pa. The specimens were placed on the sample stage of a precision xyz manipulator. The extracting field was applied between a tungsten tip and the sample. The probe tip was moved close to the sample surface by a second xyz manipulator.

The probe tip was observed through an optical microscope. The point of contact was determined by measuring the resistivity between the sample and the tip. The field emission properties were then measured at a distance of 10 μ m. The extracting voltage was increased at a rate of 30V per second until 1000V were reached. If no emission or only a small emission was obtained at first, for the activation, a high voltage was applied with the probe in contact at that position. After the activation, the emission property was measured again at the same point. When any emission current was obtained, the measurement was for the several times. A lot of series of the measurements were carried out for many times with changing the position by every several 10 μ m on the same sample. After the emission measurements, the specimen was investigated by SEM.

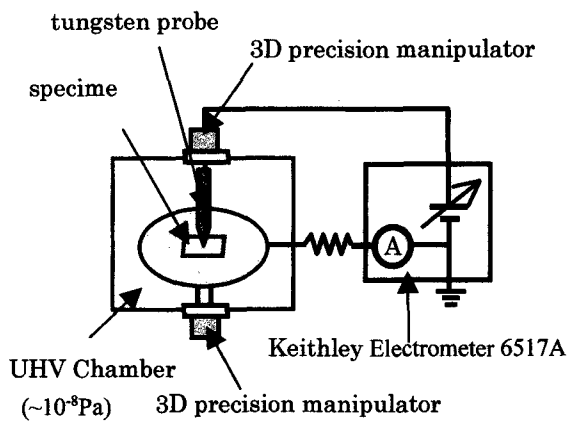


Fig. 1 Experimental set up used for electron field emission measurements.

3. RESULTS AND DISCUSSION

Figure 2 shows the Raman spectrum of the polycrystalline diamond film. The spectrum consists of the first order diamond Raman line at 1330cm^{-1} , and 2 broad bands at 1350cm^{-1} and 1550cm^{-1} due to disordered carbon. The as prepared diamond film originally emitted electrons only from some sparsely localized emission sites.

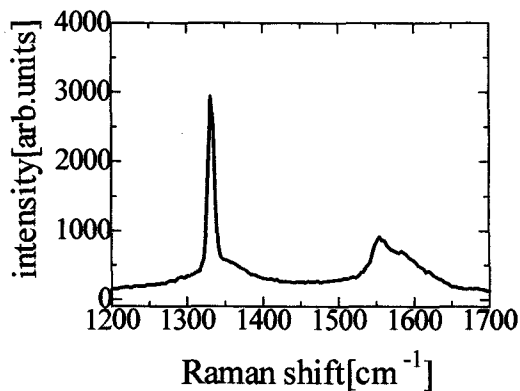


Fig. 2 shows the Raman spectrum of the polycrystalline diamond film.

It was found in the electron field emission measurements, that there were three kinds of emission behaviors as follows; (1) an original emission site of high emissivity where some morphological changes are found later by SEM observation, (2) an original emission site of low emissivity to be enhanced by applying a high electric field without any morphological changes observed after the measurements, and (3) an emission site initiated by applying a high electric field.

Figure 3 shows 3 consecutive electron field emission characteristics from an original emission point of high emissivity measured at a tip distance of $10\mu\text{m}$. The electron emission started at 500V and the emission current reached at 10^{-8}A by applying the voltage of 1000V in the first measurement, as shown by the open circles. The second and third measurements yielded

identical results with a low turn on voltage of 250V . The emission current reached at 10^{-5}A by applying the voltage of 750V . It is suggested that the original emission site is modified by the first emission measurement, and that the induced structure will be responsible for the improved emission properties and stable for electron emission during the subsequent measurement.

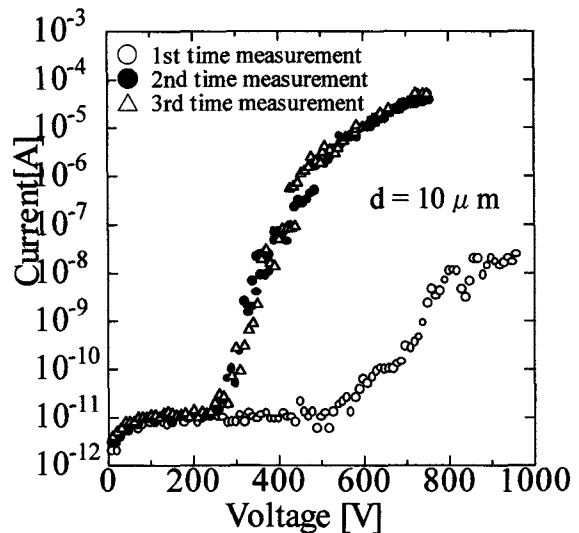
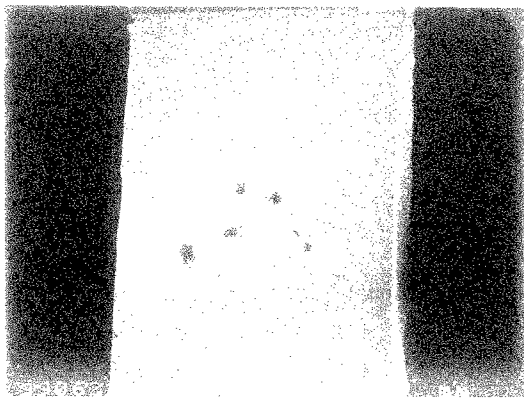


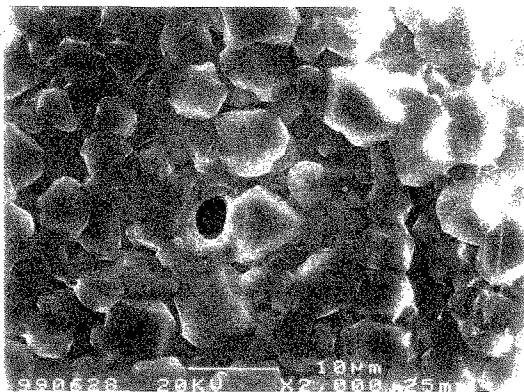
Fig. 3 Electron field emission characteristics from an original emission point of high emissivity.

Figure 4 shows a SEM image of the polycrystalline diamond film after the measurements. As a whole, the specimen looked bright possibly due to the negative electron affinity of the H-terminated diamond surface, as shown in Fig.4(a)[6]. After the emission measurements, however, some dark spots were found at some of the measured points, i.e., all of the original emission sites measured, and some of the activated emission sites. A magnified image in the dark spot is shown in Fig.4(b). It was found that a hole from 2 to $5\mu\text{m}$ in diameter had been opened in the diamond film and the surface around the hole was covered by a deposit.

In the first measurement, the electron emission happened to start at a specific position where the extracting field was focused on due to some original defects or conductive microstructures in the film. The emission current passed through the film at the original emission point. The emission current rapidly increased with increasing the extracting voltage, and the emission point was locally and rapidly heated by the first measurement resulting in burning the hole in the film. The hole was burned at the original emission point due to the local resistive heating by the emission current. The burning of the hole was also rapid and local evaporation of carbon atoms at an extremely high temperature and resulted in the deposition of a carbon layer.



(a)



(b)

Fig. 4 The SEM image of the poly-crystalline diamond films after measurement.

Figure 5 shows the I-V characteristics obtained with the probe in contact with the diamond film before and after the emission measurements. The I-V curve for the virgin film shows a Schottky behavior as indicated by the filled circles. After the electron emission measurements, the I-V characteristic became ohmic. It was due to the conductivity through the hole and the deposited carbon layer.

Figure 6 shows the electron field emission characteristics from an original emission point of low emissivity before and after applying the high electric field. As indicated by the open circles, the original site emitted electrons from 600V. The emission current reached 10^{-9} A by applying the voltage of 1000V. The plot of filled circles in Fig. 6 show the emission characteristics after the activation process of applying the high electric field. The turn on voltage decreased to 400V and the emission current increased to 10^{-7} A. By the SEM observation later, however, no change was found at these kinds of emission points.

Figure 7 shows the electron field emission characteristics of an initiated emission site. Before applying the high voltage, as indicated by the open circles, no electron emission was observed. At this point, a high electric field was applied with the probe in contact. After the activation process, electron emission

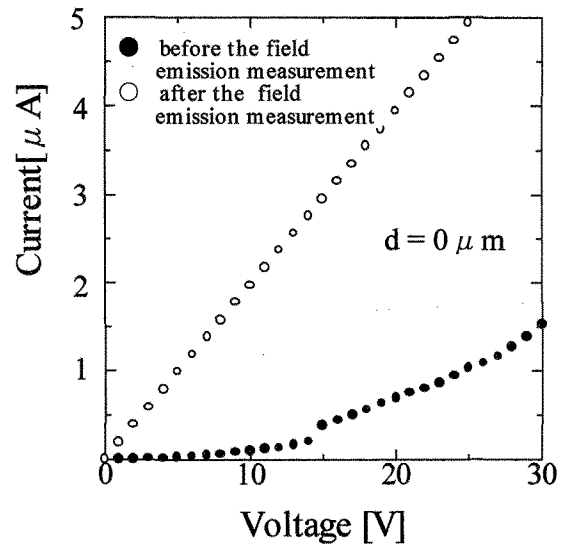


Fig. 5 I-V characteristics obtained with the probe in contact before and after the emission measurements.

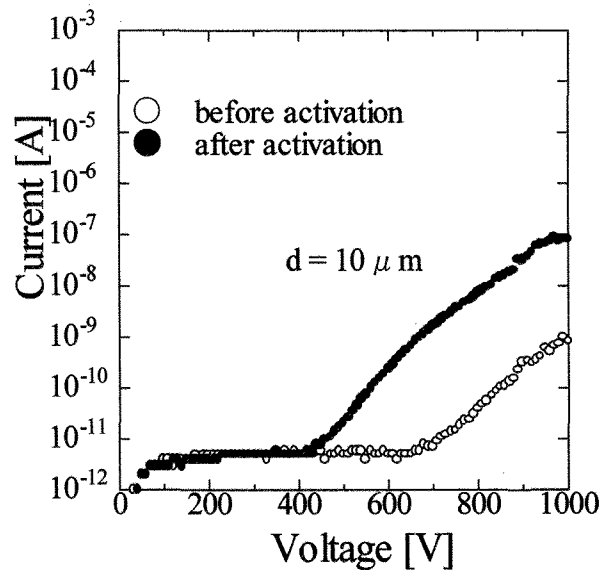


Fig. 6 Electron field emission characteristics from an original emission point of low emissivity.

started at a turn on voltage of 300V and the emission current reached 10^{-7} A at the applying voltage of 1000V. There was no remarkable change on the surface at these kinds of emission sites.

Figure 8 shows the I-V characteristics during the activation process of applying a high electric field with the probe in contact. The plot of filled circles in Fig. 8 show the activation of an original emission site which has emitted a small amount of electrons before and the emission was enhanced by the activation. The current increased continuously to 10^{-4} A with increasing the voltage. The electric current during the activation was stable and reproducible. After the activation, however, the emission property was improved. It was possibly due to resistive heating of the site resulting in modifying some microstructures in the film or on the surface which

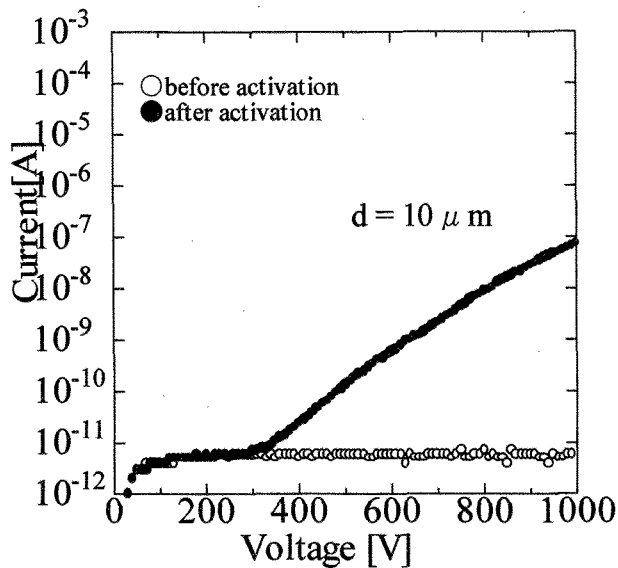


Fig. 7 Electron field emission characteristics of an initiated emission site.

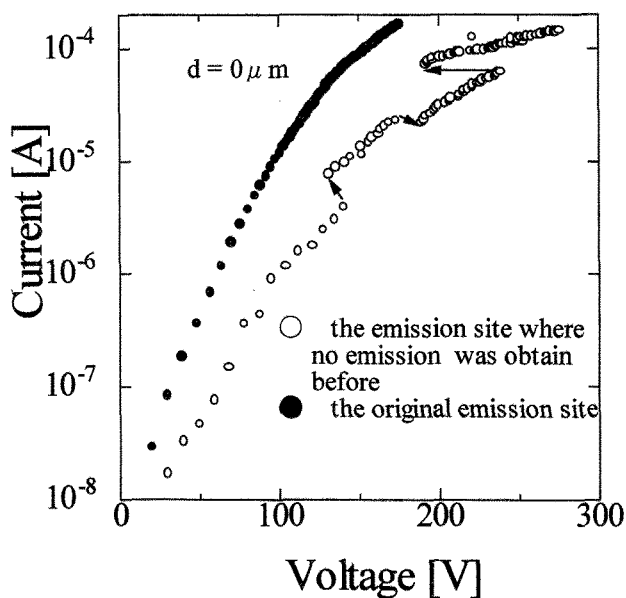


Fig. 8 The I-V characteristics during the activation process of high electric field with the probe in contact.

were not found by SEM. The open circles in Fig.8 show the I-V characteristic during the initiation of an emission site at the point where no emission was obtained before. The I-V curve for the initiation jumped several times with increasing the voltage. It can be thought that the conduction channel for the new emission site formation is not stable possibly due to movement of current pass and/or dielectric breakdown of the film. Some conductive microstructures, which are out of observation by SEM, can be induced in the film resulting in the initiation of a new emission site.

4.SUMMARY

The activation process to enhance the electron field emission from diamond films was investigated. The electron emission property of the original emission site was improved by the activation process. At the position without any original emission, a new emission site was initiated by the activation process. There was no morphological change observed by SEM after the activation. The activation seems to induce some microstructural modification in the scale out of SEM observation.

ACKNOWLEDGEMENTS

This work was supported by NEDO (New Energy Industrial Technology Development Organization) regional consortium project "Next Generation Flat Panel Display".

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(Received December 17, 1999; Accepted March 30, 2000)