

Field Emission mechanism of undoped polycrystalline diamond films

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Abstract

Field emission mechanism of undoped polycrystalline diamond films with a different amount of nondiamond carbon has been investigated using a transparent anode imaging technique and an electrolytic decoration technique. It is confirmed that for the films with a large amount of nondiamond carbon, electron transport occurs mainly through conductive grain boundaries while for the films with a small amount of nondiamond carbon, electron transports preferentially through diamond surface.

Introduction

Carbon based materials have many attractive properties such as a wide band gap, a low electron affinity, and a high chemical and mechanical stability. Therefore, researches on the carbon based materials as field emitters have been drawn extensively to enhance the electron emission properties [1-2]. Among these materials, diamond gives a high current density, a high thermal conductivity, and low field emission behaviors. Understanding the origin of low field emission is a key factor for the application of diamond to a field emitter. Many investigations have been done on the origin of low field emission. It has been reported that electron transport through substrate-diamond interfaces, electron transport through diamond films, and surface termination play an important role in low field emission [3-5]. However, electron emission mechanism is still not clearly understood.

In this study, the effect of nondiamond carbon on the transport path of field-emitted electron has been investigated using undoped polycrystalline diamond films with significantly different structural properties. Possible electron transport paths and field emission mechanism for undoped polycrystalline diamond films are discussed.

Experiments

Undoped polycrystalline diamond films were deposited on Si substrates (*n*-type (100), 0.015 Ω cm) by a hot filament chemical vapor deposition (HFCVD) method using a mixture of methane and hydrogen gases. In order to modify the nondiamond carbon content in diamond films, the flow ratios of CH₄ to H₂ gas were varied from 2% to 15%. The total gas flow rate was fixed at 100 sccm during the deposition procedure, except for the 15% CH₄ concentration with a total flow rate of 67 sccm. The filament temperature, the substrate temperature, and the total gas pressure were fixed at 2000 °C, 850 °C, and 15 torr, respectively. In order to confirm the field emission mechanism, diamond films were selectively deposited on a Si substrate covered with a Mo plate.

The field emission property was measured in a vacuum of $\sim 5 \times 10^{-9}$ torr. The distance between the anode and the cathode was kept at ~ 100 μ m. A Keithley 248 voltage supply was used to apply the voltage to the anode. The I-V data were taken using a computer-controlled Keithley 487 picoammeter through an IEEE-488 interface. In order to visualize the spatial distribution of the emission sites, we have used a phosphor coated ITO glass as an anode. In order to identify the electron transport path through the diamond films we have used an electrolytic decoration technique. The solution was a CuSO₄ saturated deionized water. A copper

plate was used as an anode and diamond surfaces were used as a cathode. A voltage of 10 V was applied for 10 min. The structure and morphology of the diamond films were examined by micro-Raman spectroscopy and scanning electron microscopy.

Results and Discussion

Table 1 shows the turn-on and threshold fields of the films deposited at 2%, 5%, 10%, and 15% CH₄. The turn-on field and threshold field are defined as the field for a current of 1 nA/cm² and 1 μ A/cm², respectively. Increasing the CH₄/H₂ ratio from 2% to 5% and 10% significantly reduces the turn-on and threshold fields, except that the film grown at 15% CH₄/H₂.

Figure 1 shows the spatial images of emission sites for the films with a different amount of nondiamond carbon. The sample #1 with a relatively small amount of nondiamond carbon shows only a few emission sites, which are predominantly positioned at the edge (Fig. 1(a)). As the CH₄/H₂ ratio increases to 5 and 10%, the image (Fig. 1(b) and (c)) shows that the total number of emission sites increases significantly and the emission sites are observed at the center as well as at the edge of the sample. In contrast, when the CH₄/H₂ ratio increased to 15% the number of emission sites starts to decrease.

The important finding is that the field emission property and emission patterns depend strongly on the nondiamond carbon content, except for the film grown at 15% CH₄/H₂; an increase of the nondiamond carbon content in diamond film leads to the lower turn-on and threshold field and the change of emission sites from the edge to both the edge and the central region. One could surmise from these results that there would be two kinds of transport paths for field-emitted electrons.

One is that electrons transport through the diamond surface. Since the diamond films are deposited on four sides of the Si substrate as well as on the Si substrate surface, and the Mo plate is contacted with the diamond films using silver epoxy, a triple junction is formed at the metal-diamond-vacuum interface, similar to the metal-insulator-vacuum triple junction [6]. In this

Table I. Deposition conditions and field emission properties of the undoped polycrystalline diamond films.

Sample	CH ₄ /H ₂ ratio, growth time	E _{turn-on} (V/ μ m)	E _{threshold} (V/ μ m)
#1	2%/2 h	10.4	14.9
#2	5%/1 h	6.5	8.5
#3	10%/1 h	2.8	3.6
#4	15%/1 h	5.0	6.8

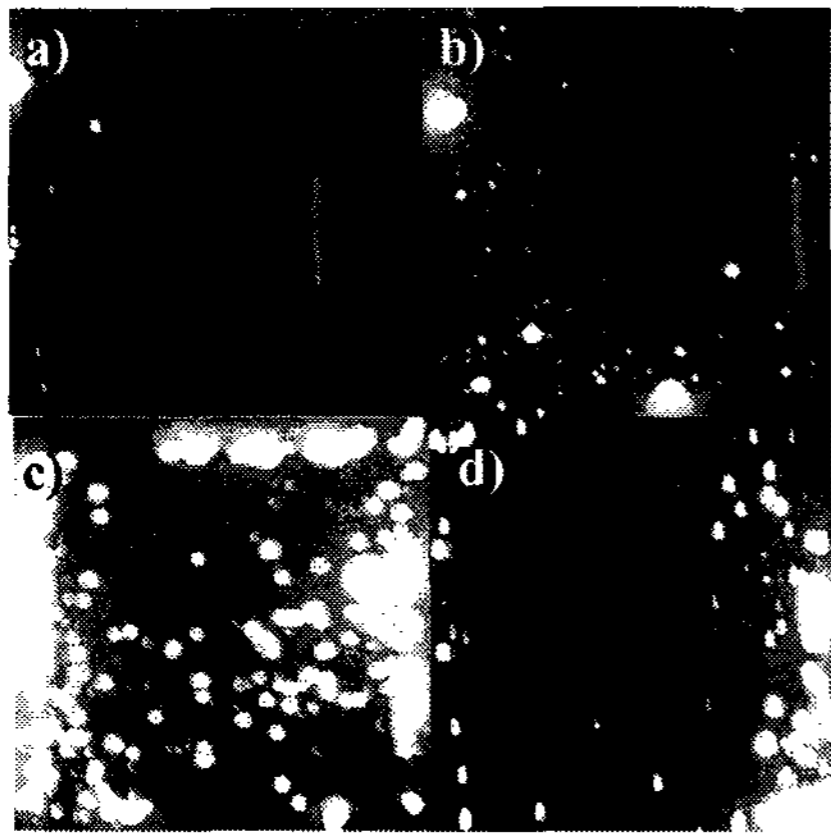


Figure 1. Spatial distributions of emission sites as recorded from the diamond samples. The field is (a) 20 V/ μm (#1), (b) 10.8 V/ μm (#2), (c) 10.6 V/ μm (#3), and (d) 10.6 V/ μm (#4).

case, electron tunneling at the triple junction transports through the diamond surface by hopping and finally escapes into a vacuum. In this respect, the observed predominant edge emission phenomenon shown in Fig. 1 (a) can be explained by the surface electron-emission that occurs by a substantial field enhancement at a metal-insulator-vacuum triple junction [5].

In order to confirm the edge emission phenomenon, diamond films were selectively grown on a Si substrate ($1.2 \times 1.2 \text{ cm}^2$) covered with a Mo mask ($1 \times 1 \text{ cm}^2$) that has a hole ($0.5 \times 0.5 \text{ cm}^2$). The low resistivity *n*-type Si substrates could be considered as a good conductor because they were heavily doped. Therefore, triple junctions at the Si-diamond-vacuum interface are formed at the four sides of the two regular tetragons. The spatial image (Fig. 2(a)) of the diamond films deposited at 5% CH_4/H_2 shows that the luminescence is observed only at the sides of the tetragons. In addition, there has been no emission site from the interior surface of the patterned diamond films while those were observed in the unpatterned diamond films in Fig. 1(b). This result reflects that a considerable field enhancement occurs at the triple edge. Figure 2(b) shows the image of the diamond films grown at 2% CH_4/H_2 . In this sample, island-type diamond was grown on the underneath of the Mo mask because the Mo mask was slid during deposition procedure, while a continuous diamond film was grown on the hole and on the outside of the hole. Thus, Si surface-island diamond-vacuum interfaces act as numerous triple junctions. As shown in Fig. 2(b), at a substantially low field of 7 V/ μm , a fully brightened emission image is observed at the region with island-type diamond as well as the four sides of the two regular tetragons. Therefore, it is concluded that the emission phenomenon observed in Fig. 1(a) and Fig. 2(a) and (b) is attributed to the surface emission.

The other is that electrons preferentially transport through

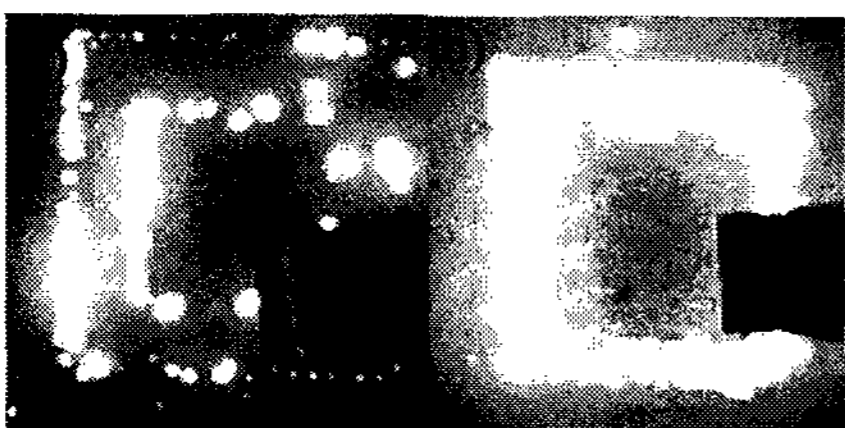


Figure 2. Spatial distributions of emission sites recorded at (a) 13 V/ μm (5% CH_4/H_2) and (b) 7 V/ μm (2% CH_4/H_2).

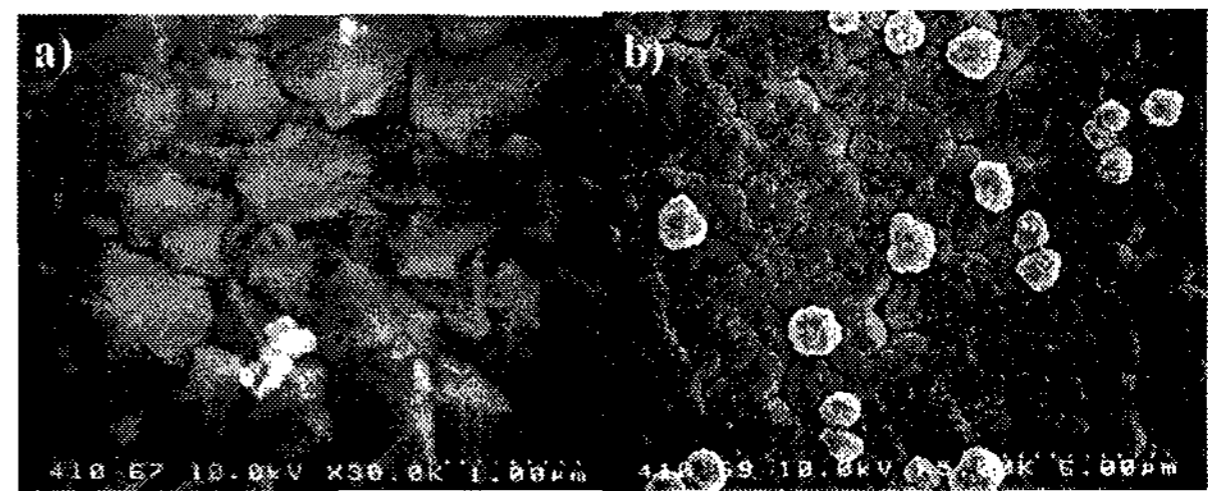


Figure 3. SEM photographs of a copper decorated surface of the diamond films grown at the CH_4/H_2 ratio of (a) 2 % and (b) 5%.

the grain boundaries. Polycrystalline diamond film has grain boundaries that consist of conductive sp^2 bonding [7]. Also, it has been reported from the result of micro-Raman spectroscopy that the conductive graphite-like phases are mainly segregated on the grain boundary [8].

In order to clearly confirm the dominant electrical transport path in undoped polycrystalline diamond films, we have used an electrolytic decoration technique. Figure 3 shows typical photographs of the samples grown at 2% and 5% CH_4/H_2 . Few small white particles are observed in the sample grown at 2% CH_4/H_2 which exhibits the edge emission phenomenon. The Cu has been deposited electrolytically on the spots that have electrical current path through the grain boundary. It should be also noted that more particles with a larger size are deposited on the grain boundaries of the sample #2 with a larger amount of nondiamond carbon. This result indicates that electrons transport through grain boundary, rather than the grains. Consequently, the electrons arrived at the grain boundary-vacuum interface are field-enhanced since the grain boundary-diamond-vacuum interface structure is similar to the metal-insulator-vacuum triple junction. Finally, the electrons at the junctions tunnel directly into a vacuum or into the surface of semi-insulating diamond matrix. From the present investigation, it is concluded that the variation of nondiamond carbon content in undoped polycrystalline diamond films decides the electron transport path and the resulting field emission mechanism.

Conclusion

We have shown that electron transport path depends strongly on the nondiamond carbon content in undoped polycrystalline diamond films by examining the spatial distribution of emission sites and the electrolytic decoration method. It is thus concluded that electrons transport preferentially through the conductive grain boundaries for the film with a large amount of nondiamond carbon, while electron transport occurs mainly through the diamond surface for the film with a relatively small amount of nondiamond carbon.

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