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Scanning probe field emission current measurements on diamond-like carbon films treated by reactive ion etching

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Abstract

Nitrogen-doped chemical vapour deposited diamond-like carbon (DLC) films were treated by reactive ion etching system under various conditions of CHF₃ gas successively after pre-treatment with oxygen. Atomic force microscopy and Raman spectroscopy were carried out in order to characterize the surface morphology and chemical bond, respectively. Scanning tunnelling microscopy was used in order to investigate the surface state of the DLC films at the nanoscale level. Scanning probe field emission current measurement was performed in order to obtain the emission current mapping. The emission sites appeared to a great extent after the surface treatment by CHF₃ gas and a clear activation effect was observed. We confirmed that the surface treatment using CHF₃ gas affected not only the appearance of emission sites but also the activation process.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Diamond-like carbon (DLC) is an amorphous structure composed of a network of tetrahedrally coordinated sp³ bonds and trigonally coordinated sp² bonds. DLC is a promising material in a wide range of fields due to its advantages such as mechanical hardness, dielectric strength,

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chemical inertness, low wear and friction and optical transparency [1–5]. In particular, there have been numerous reports on the field emission properties of DLC for the application to a cold cathode material of field emission displays (FEDs). A field emission from a DLC surface at a low electric field [6] has been expected because of its similar properties to diamond [7–9]. However, there has been no report on the exact value of the electron affinity of DLC, though there have been reports that the electron affinity is low [10, 11]. On the other hand, the field emission mechanism from the DLC surface has not yet been clarified. Experimental results of field emission have been split into the effect of the physical microstructure such as the surface roughness [12–14] and local enhancement of the electric field [14, 18], or the effect of a chemical bond on the DLC surface such as impurity doping [15] and the ratio of sp^3 to sp^2 bonding. Milne *et al* [16] confirmed the improvement of the field emission property from the sp^3 -rich ta-C film treated by hydrogen and oxygen. We carried out the surface treatment of nitrogen-doped DLC films by reactive ion etching (RIE) with oxygen gas in order to change the surface morphology [17]. The increase in surface roughness was observed by AFM and also the improvement of the field emission property was confirmed. However, the increase in bond ratio of oxygen and carbon on the DLC surface was observed by x-ray photoemission spectroscopy (XPS) measurement. We had some misgivings about a bad influence of the O–C combination in the bulk on the field emission property, because Robertson *et al* [10] reported that the oxygen termination gave a large positive electron affinity.

In this work, the surface treatment using CHF_3 gas is carried out in addition after the oxygen treatment. Scanning probe methods are performed in order to obtain the surface morphology image and emission current mapping. The emission sites on DLC films usually distributed randomly. However, the number of emission sites obviously increases after the surface treatment using CHF_3 gas. It is demonstrated that CHF_3 plasma treatment followed by the activation process is a useful way for FEDs application.

2. Experimental procedure

We deposited nitrogen-doped DLC films of approximately 200 nm thickness on a (100) n^+ -Si substrate by using the radio frequency plasma-enhanced chemical vapour deposition (rf-PECVD) system. An rf-power of 13.56 MHz was applied between the electrically grounded anode and water-cooled cathode. The substrates were set on the cathode. We used a mixture of methane and nitrogen gas as a source. The total gas pressure was maintained at 10 mTorr with nitrogen gas pressure of 3 mTorr. The negative self-bias voltage was fixed at 1300 V. As-deposited DLC film had a very smooth surface.

A reactive ion etching (RIE) system was employed to treat the surface of the DLC films. DLC films were treated by oxygen plasma at first in order to change the surface morphology. Next CHF_3 plasma treatment was done successively in the same chamber. In this work, the conditions of the oxygen plasma pre-treatment were fixed at 20 W rf power, 1 Pa gas pressure and 10 min treatment time.

Raman spectroscopy was used for characterization of the chemical bond. Field emission properties were investigated under various conditions of CHF_3 plasma treatment using scanning probe methods. Atomic force microscopy (AFM) was used to observe the surface morphology over a region of $1 \times 1 \mu m^2$ and the roughness R_{ms} was calculated by a root mean square method. Scanning tunnelling microscopy (STM) was used in order to observe the surface structure and electronic state of the DLC surface after the treatment by CHF_3 gas. The vacuum level in the main chamber was maintained at lower than 3×10^{-8} Pa.

Scanning probe field emission current (SPFEC) measurements were carried out in high-vacuum (lower than 3×10^{-6} Pa) to obtain the emission current mapping images in the region

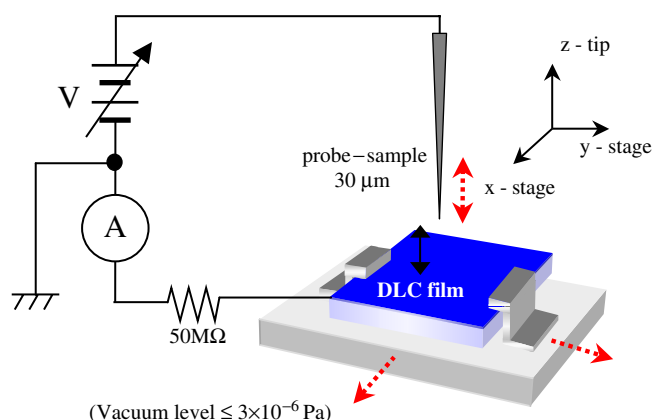


Figure 1. A schematic diagram of the scanning probe field emission current (SPFEC) set-up.

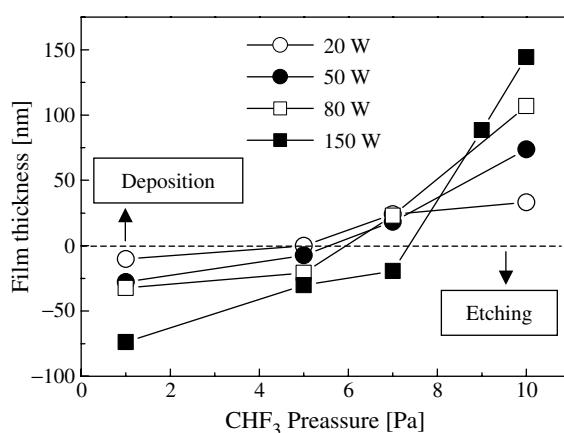


Figure 2. Film thickness versus CHF₃ pressure.

of $2 \times 2 \text{ mm}^2$. A schematic diagram of the SPFEC set-up is shown in figure 1. The spacing between the probe and sample surface was kept at $30 \mu\text{m}$ and a constant dc bias voltage was applied to the tip during the probe scan. It is reported that the field emission property of DLC films can be enhanced after the application of a high electric field due to activation [18, 19]. The applied voltage was increased from 2000 to 4000 V in order to ascertain the activation effect. The field emission I - V characteristics were also measured by using a parallel plate electrode of an indium tin oxide (ITO)-coated glass, spaced $100 \mu\text{m}$ with Teflon sheet from the DLC surface. The emission current was measured by applying a voltage up to 4000 V more than five times to stabilize the current fluctuation.

3. Results and discussion

After the deposition of DLC on a silicon substrate, the surface was partially covered with a glass plate during CHF₃ plasma treatment in order to measure the thickness removed by RIE. The step at the coverage was measured by α -step. The results are plotted in figure 2 for

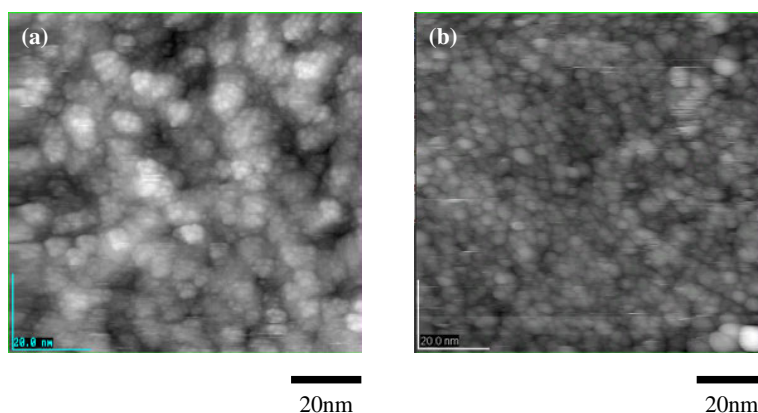


Figure 3. STM images of a DLC film treated by oxygen with 1 Pa, 20 W, 10 min (a) and subsequently treated by CHF₃ gas with 5 Pa, 80 W, 10 min (b).

various CHF₃ pressures. This shows that the etching process occurred under a CHF₃ pressure less than 5 Pa. On the other hand, under a pressure more than 5 Pa, deposition occurred. Since CHF₃ gas contains a CH-bond, both etching and deposition are originated in the same plasma circumstance, depending on the source gas pressure. Some polymer-like film must be deposited under high CHF₃ pressure.

Figure 3 shows STM images of a DLC film treated by oxygen (1 Pa, 20 W, 10 min) and subsequently treated by CHF₃ gas (5 Pa, 80 W, 10 min), over a region of 80 × 80 nm². It can be seen that the grain size for the CHF₃ case (b) is smaller than that of the oxygen case (a). The measurement conditions were sample bias of 4 V and tunnelling current of 0.2 nA (a) and 0.07 nA (b).

Figure 4 shows AFM images of oxygen-treated and CHF₃-treated DLC films. The treatment conditions for CHF₃ were 5 Pa, 80 W and 10 min. The root mean square roughness R_{ms} obtained by calculating the average of three regions was 0.46 nm for the oxygen treatment and 0.37 nm for the CHF₃ treatment, respectively. Both STM and AFM measurements showed the surface roughness of DLC films decreased after CHF₃ treatment.

Figure 5 shows typical Raman spectra of DLC films after the oxygen treatment (a) and after the subsequent CHF₃ treatment. As-deposited DLC showed a similar spectrum to the oxygen case in figure 5(a). The ratio of D peak intensity to G peak intensity $I_{\text{D}}/I_{\text{G}}$, and the G peak position shift versus treatment time are plotted in figure 6. The CHF₃ treatment conditions were 5 Pa gas pressure with 80 W rf-power. The ratio $I_{\text{D}}/I_{\text{G}}$ increased and the G peak position shifted from 1580.7 down to 1577.1 cm⁻¹ with increasing treatment time. This might be explained by the disordering and high sp³/sp² ratio. Also the G band became wider, which indicates an increase in defect density and decrease in domain size on the surface structure.

Figure 7 shows the SPPEC mapping images of the DLC surface modified by CHF₃ plasma, where 2000 V was applied with a spacing of 30 μm over a region of 2 × 2 mm² the second time. There were a few emission sites at the first scan of 2000 V. However, the numerous appearances of emission sites were confirmed at the second scan after the activation, as shown in figure 7(a). In the figure, the current value in the white area is more than 20 μA at high emission sites and in the coloured area the current value is less than 1 pA. The emission current for the CHF₃ treatment was stable and much higher than that for the oxygen treatment. Figure 7(b) is the current mapping obtained after movement in both the *x* and *y* directions by 500 μm. We can see a clear activation effect as happens with diamond. Even an optical

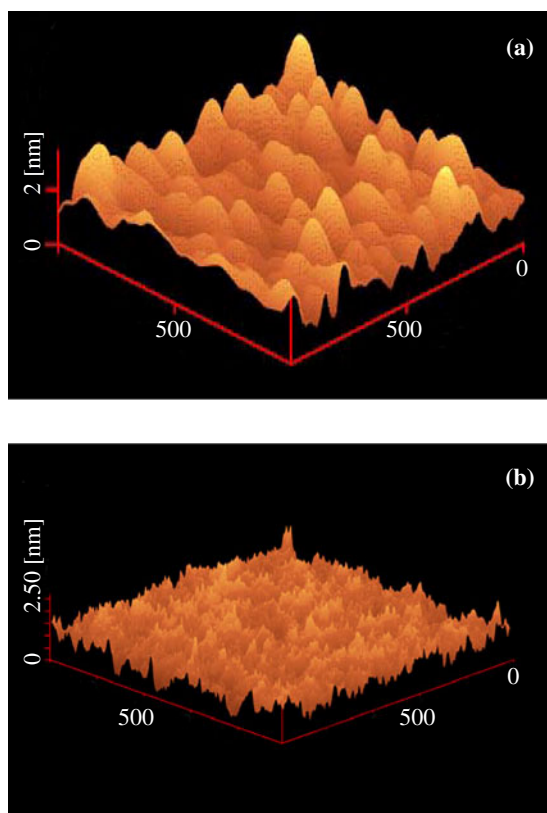


Figure 4. AFM images over a region of $1 \times 1 \mu\text{m}^2$. Oxygen treatment, $R_{\text{ms}} = 0.37 \text{ nm}$ (a) and subsequent CHF_3 treatment, $R_{\text{ms}} = 0.46 \text{ nm}$ (b).

microscope inspection showed some visible damage after the application of a high voltage for a long time. The activation effect is known to be non-destructive and reproducible [1].

Figure 8 shows the result of SPFEC and the local $I-V$ characteristics on a DLC film. The plasma treatment conditions are the same as in figure 7. The threshold voltage in high emission sites (e, d) was low compared with the non-activated points (a, b, c). This means that there is, as perceived by the mapping image, some close relation between the activated site and the mechanism of field emission.

Figure 9 shows the field emission $I-V$ characteristics measured with parallel plate configuration. The CHF_3 treatment condition was 5 Pa and 80 W. It can be seen in figure 9 that the threshold electric field is the lowest at 10 min treatment; it does not show any apparent change with time after 10 min treatment time.

Since the surface roughness decreased after CHF_3 treatment, the emission property should not depend on the morphology. The emission current increased after the CHF_3 treatment and showed an activation effect like diamond. It is considered that CHF_3 treatment makes C-F bonding at the surface and removes C-O bonding. However, a long treatment (more than 10 min at 5 Pa) did not improve the threshold field. It is seen in figure 2 that 5 Pa is close to the critical pressure where the mode of etching and deposition changes. Some polymer-like layer might be deposited after more than 10 min, revealing no change of the threshold field in this case.

As a result, CHF_3 treatment for 10 min is effective for both the appearance of emission sites and the activation process. It is considered that some polymer-like films are deposited

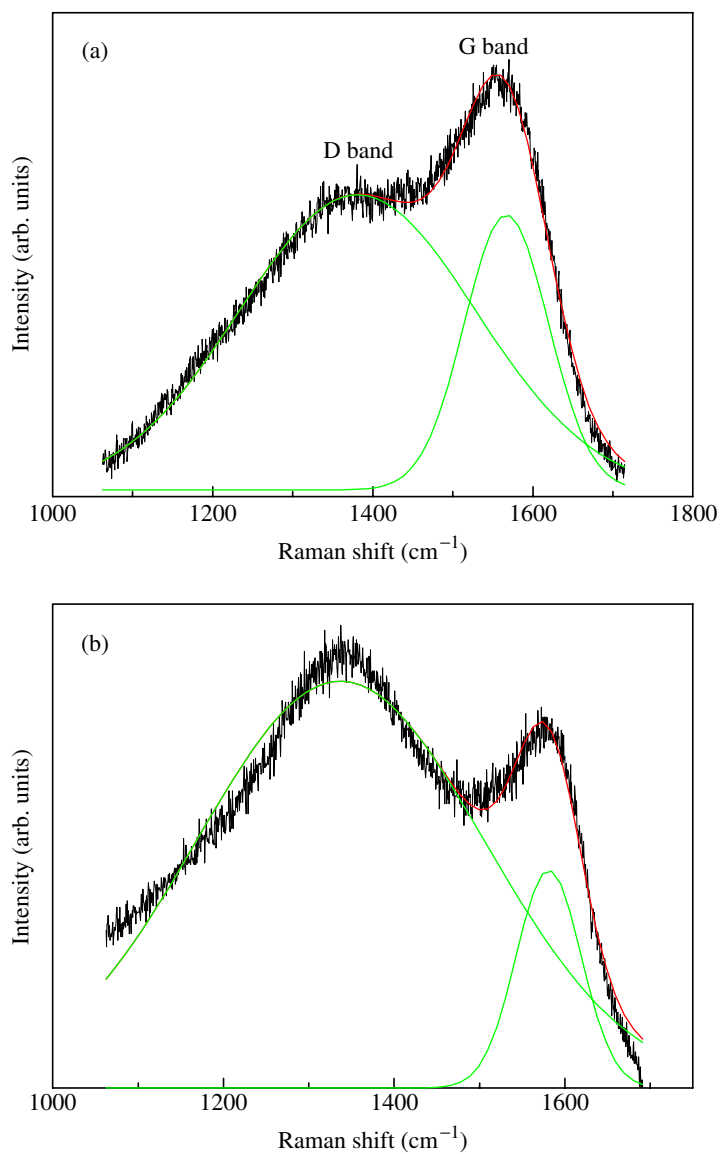


Figure 5. Raman spectra of DLC films after oxygen treatment (a) and after subsequent CHF₃ treatment (b).

after CHF₃ treatment under high pressure. XPS and other measurements will be necessary to clarify the nature of the surface bond after CHF₃ treatment.

4. Conclusion

We investigated the effect of CHF₃ plasma treatment of DLC films on field emission properties. The surface treatment by CHF₃ gas was performed successively after oxygen plasma treatment in order to change the surface morphology and improve the emission characteristics. As the CHF₃ pressure increased, a mode change from etching to deposition occurred. The surface

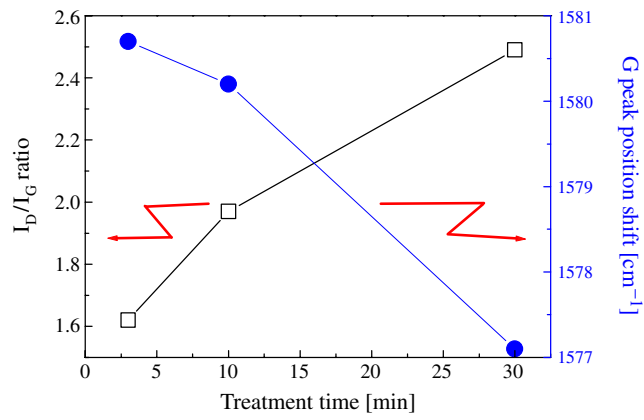


Figure 6. I_D/I_G ratio and G peak position shift versus treatment time. CHF_3 treatment: 5 Pa, 80 W.

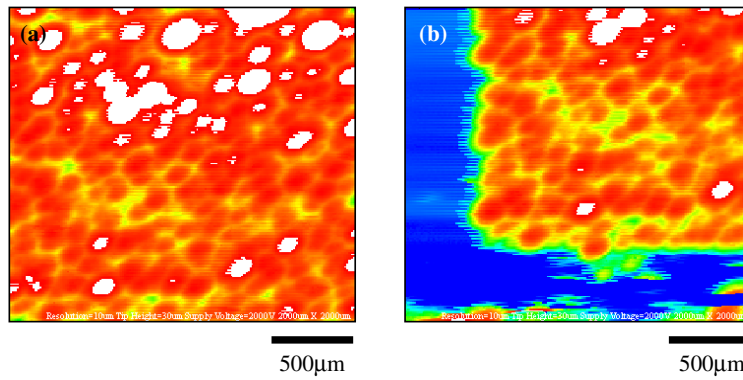


Figure 7. SPFEC mapping images at 2000 V over a region of $2 \times 2 \text{ mm}^2$. (a) The second scan after the activation and (b) the third scan after movement in both the x and y directions by $500 \mu\text{m}$. Pre-oxygen treatment: 1 Pa, 20 W, 10 min; CHF_3 treatment: 5 Pa, 80 W, 10 min.

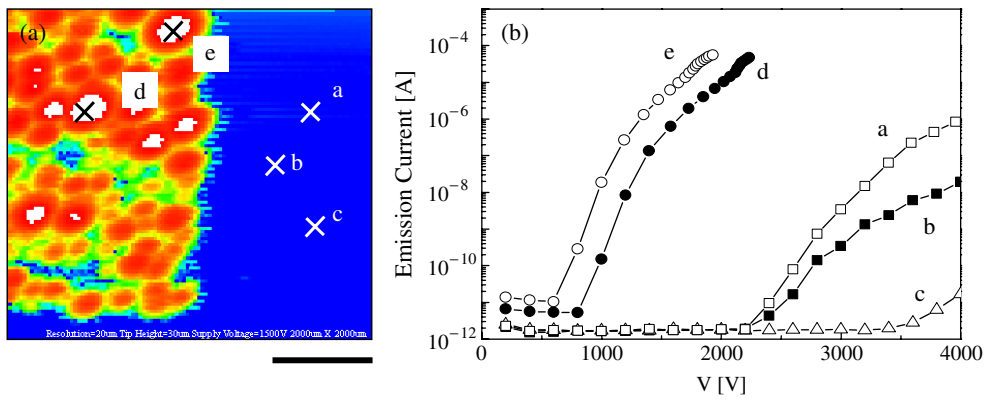


Figure 8. SPFEC mapping (a) and I - V characteristics (b) of DLC films. The plasma treatment conditions of oxygen and CHF_3 are the same as those in figure 6.

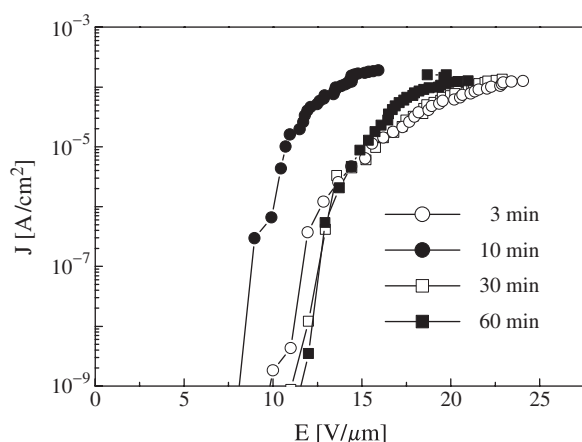


Figure 9. Field emission I - V characteristics measured by a parallel plate configuration. Pre-oxygen treatment: 1 Pa, 20 W, 10 min; CHF_3 treatment: 5 Pa, 80 W.

roughness after CHF_3 treatment decreased, while the D peak in the Raman spectrum which corresponds to disordering increased. The field emission property of CHF_3 treated DLC films measured by SPFEC showed an activation effect like diamond. After the activation, the current increased and became stable. For a parallel plate configuration, the current density showed the lowest value after 10 min treatment. Some polymer-like layer might be deposited with longer time treatment. XPS and other measurements will be necessary to clarify the nature of the surface layer.

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