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Field emission from diamond-like carbon films studied by scanning anode

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Abstract – We deposited diamond-like carbon (DLC) films using ion beam sputtering of a graphite target on flat substrates for use as a thin film field emitter. An n-type silicon wafer, titanium-coated silicon, and indium tin oxide (ITO)-coated glass were used as a substrate. All films exhibited a sudden increase in the emission after a breakdown occurred at high voltage. The morphology of the films after the breakdown depended on the substrate. On ITO and Ti substrates, the DLC film peeled off upon breakdown, but on the Si substrate the surface melting due to breakdown resulted in the formation of various structures such as a sharp point, mound, and crater. By scanning the deformed surface with a tip anode, we found that the emission was concentrated at the deformed sites, indicating that the field enhancement due to the morphology change was responsible for the increased emission.

I. Introduction

Diamond films, because of their hardness, stability, thermal conductivity, and possible negative electron affinity [1, 2] exhibit a great potential for application as an electron emitter for vacuum microelectronics. Growing diamond films requires a high temperature process, however, whereas a diamond-like-carbon (DLC) film can be deposited at mild temperatures even though it exhibits similar properties as a diamond film. Therefore, there is a considerable motivation to use DLC as a thin film field emitter. DLC films show different properties depending on the growth condition. As for field emission properties, DLC films containing both sp^3 and sp^2 bonds are believed to be better than those containing only sp^3 bonds [3, 4]. This was attributed to the abundance of sp^3 clusters acting as emission sites embedded in the sp^2 matrix which acted as a conductive path. On the other hand, hydrogen atoms in a DLC film made by chemical vapor deposition (CVD) is known to remove the unpaired bonds eliminating the conducting path inside the film, and also hydrogen desorbs easily to increase the local pressure between the emitter and the anode. Deposition using laser ablation can produce a hydrogen-free DLC film, but the surface is very rough and it is difficult to get a uniform emission [5]. We deposited hydrogen-free DLC films on flat substrates using an ion beam sputtering method. In this method, the first ion gun sputters a graphite target for DLC deposition and the second gun can inject ions into the deposited film. The resulting films were smoother than laser ablation-deposited films but rougher than CVD films. From the films we deposited, however, it was difficult to get the emission current unless a breakdown occurred at the increased bias voltage, which is similar to the previous reports. We also had to cycle the bias voltage in order to get the measurable emission. In this case, the breakdown was not noticeable during the *I-V* measurement, but could be confirmed from the change in the surface morphology under the scanning electron microscopy after the measurement. In order to understand the role of the morphology change, and compare the emission before and after the arcing, we measured the local emission by scanning a point anode and the local composition using spot Auger spectroscopy. The measurements showed that the emission was concentrated at the sites deformed by arcing, and Si, C, and SiC were detected from the deformed sites.

II. Experiment

DLC films were deposited using a [illegible]al ion beam sputtering system [6]. The base pressure of the coating chamber was 5×10^{-6} Torr. Before deposition, substrates were sputter-cleaned by direct argon ion beam (15 mA at 400 V) for 1 min under the pressure of 3×10^{-4} Torr. For the DLC deposition, the argon ion beam energy was set at 1000 eV. The film thickness was controlled by the deposition time, and we chose 20, 40, and 60 min deposition for the present study. The pressure after filling the chamber with argon for the DLC deposition was 3.5×10^{-4} Torr. For the nitrogen implantation into the DLC film, we injected a nitrogen ion beam toward the substrate using a second ion gun. To compare the effect of the substrate on the emission, we deposited DLC on a Ti-coated glass plate, indium tin oxide (ITO)-coated glass, and Si wafer. The emission current was measured in a vacuum of 4×10^{-7} Torr. To measure the emission, a stainless steel ball of 6 mm in diameter was used as an anode. The anode was placed 50 μm above the DLC surface and the bias voltage was applied between the anode and the sample. To map the local emission, we scanned the surface with a point anode while keeping the distance and the voltage constant. The point anode was a sharp tip made by electrochemical etching of a tungsten wire. The cathode-anode gap distance was kept at 30 μm as checked with a high magnification CCD camera, and the bias was kept constant at 500 V. The scanning anode tip was made by electrochemical etching of a tungsten wire. The tip was attached to a micrometer and scanned manually with a step distance of 2.5 μm for both x and y directions. The films were also analyzed using scanning electron microscopy, scanning Auger electron spectroscopy, and micro-Raman spectroscopy.

III. Results and Discussion

When the voltage was applied to measure the *I-V*

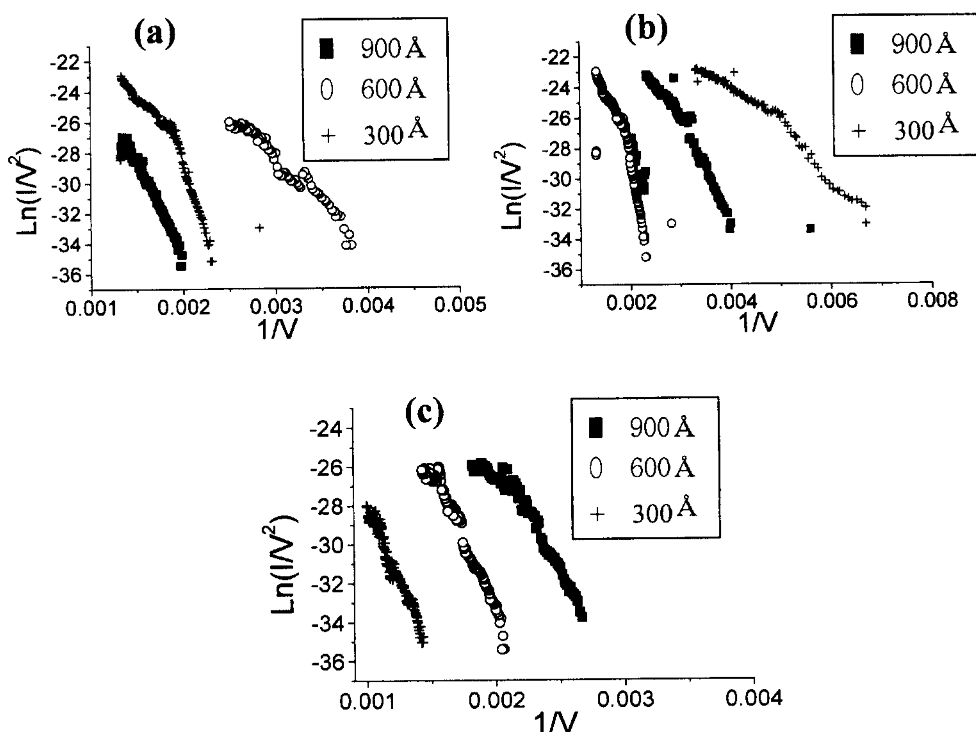

Fig. 1. Fowler-Nordheim plots of the representative *I-V* data obtained after the arcing at high bias voltage. The samples were a DLC film grown on (a)Ti substrate, (b) ITO-coated glass substrate, and (c) n-type silicon substrate. DLC films of different thickness were tested, but the emission after the arcing did not show a dependence on the thickness.

curve for the first time, the emission current was difficult to get. The noticeable current was observed after the bias voltage was cycled several times or an arcing occurred at high voltage, which is similar to the previous report [4]. Representative Fowler-Nordheim plots of the emission data obtained from the DLC films after the arcing at over 2 kV are shown in Fig. 1. The thicker the dielectric film is, the lower the emission will be because of the increased resistance, but as shown in the data, the emission enhanced by arcing does not show a characteristic trend regarding the DLC thickness. This means that once the morphology is changed by arcing the thickness of the film is not an important parameter for the emission. Although the emission was observed from the DLC films grown on all three different substrates, the emission was very noisy and unstable in case of the Ti and ITO substrates.

Fig. 2. SEM micrographs of the sites damaged by arcing. The morphology is different depending on the (a) Ti, (b) ITO-coated glass, and (c) n-type silicon substrates. On the Ti and ITO substrates, one can see the DLC debris. On the Si substrate, the surface melting caused the mixing of Si and C.

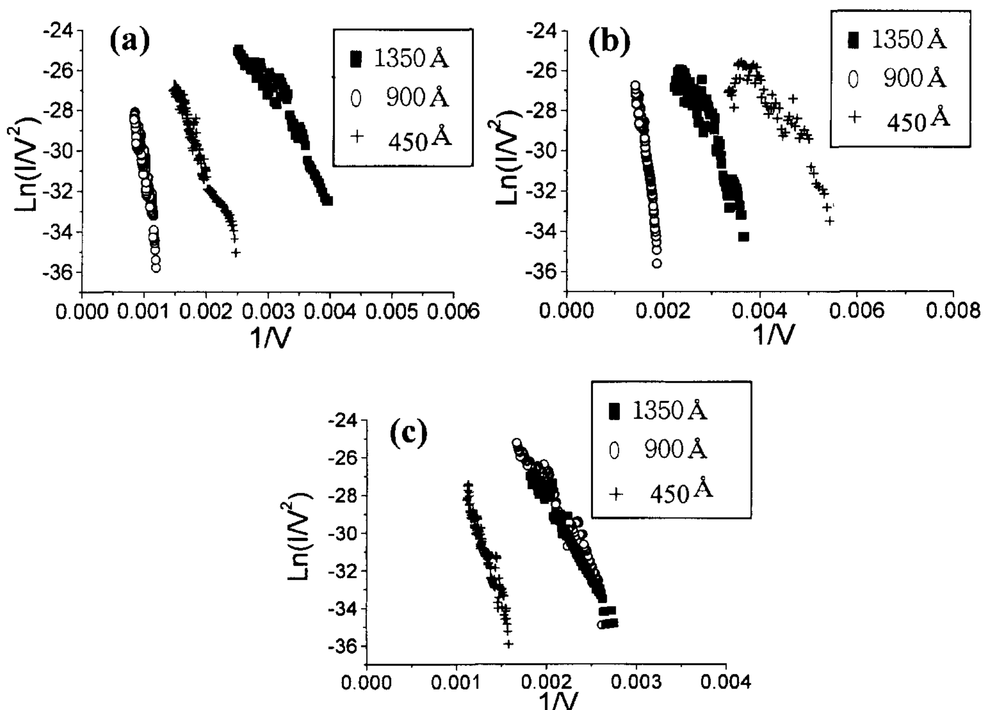

Fig. 3. Fowler-Nordheim plots of the emission data measured from nitrogen-incorporated DLC films grown on (a) Ti, (b) ITO-coated glass, and (c) n-type silicon substrates. Similarly to the nitrogen-free samples, the emission could be observed after the voltage cycling or the arcing at high voltage.

The reason for this can be explained with the SEM micrograph of the samples displayed in Fig. 2. When the arcing or microdischarge occurs, the DLC film peels off from the Ti and ITO surfaces and flutters when the electric field is applied. Because of this, the current, which is emitted from the edge of the peeled-off film, is very unstable. In the case of ITO, a shallow crater is also formed at the center of the deformed site, but this is not shown on the Ti substrate reflecting the high melting temperature of Ti. Peeling of the DLS film from Ti and ITO substrates is due to the weak adhesion. The morphology after arcing is quite different on the Si substrate. In Fig. 2(c), one sees that DLC and Si melted together and formed a structure different from those on the Ti and ITO substrates. Once we achieved the emission current from the DLC/Si by cycling the voltage or by inducing breakdown, the emission was relatively stable and reproducible if the voltage was kept low so as not to induce another breakdown.

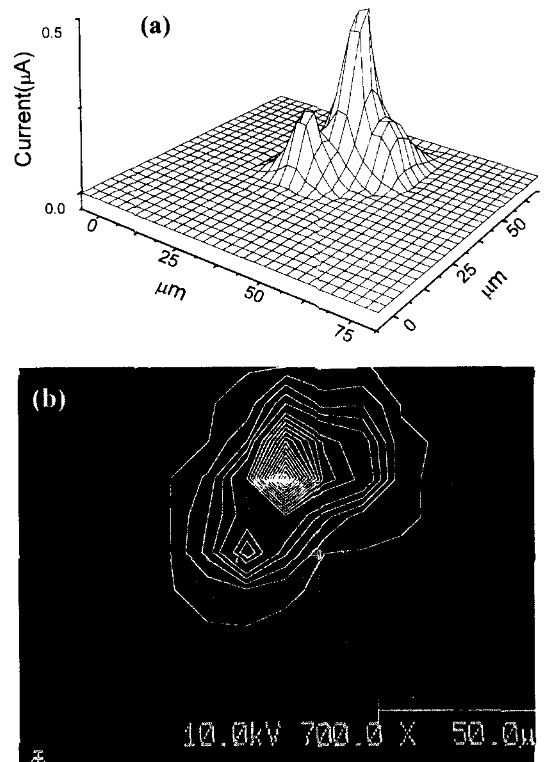

Fig. 4. (a) 3-dimensional view of the distribution of the local emission current over the surface of DLC-coated Si wafer. The current is shown to be localized at the deformed site. (b) SEM micrograph of the deformed site superposed with the emission map. The current peaks are located at the edge of the creater.

Nitrogen impurity in diamond and DLC is known to increase the bulk conductivity through the n-type doping effect. Okano *et al.* reported that nitrogen incorporation into diamond also increased the electron emission [7]. In order to incorporate the DLC film with nitrogen, the film was exposed to nitrogen ion while it was being grown. The emission measurement of these films yielded the same result as the nitrogen-free samples, i.e., the emission was possible after the voltage cycling or after the arcing at high voltage. Fowler-Nordheim plots of the representative *I-V* data from the nitrogen-dosed DLC films are displayed in Fig. 3, but the emission curves are not much different from the undoped films shown in Fig. 1. The SEM micrographs of the defect morphology created by arcing was also similar.

Two parameters that determine the electron tunneling are the material work function and the local electric field. The work function of DLC films is often estimated from the Fowler-Nordheim plot, and the result is unexpectedly low [8]. If an emitter is 3-dimensional, however, an uncertainty rises because based only on the Fowler-Nordheim equation one cannot differentiate the role of work function from the alteration of electric filed due to surface morphology change. Since the electron emission became possible when the surface morphology changed with arcing, we expected that the emission be localized at the deformed sites. This is confirmed by Fig. 4, which are the 3-dimensional view of the emission map and the superposition of the SEM micrograph and the map of the local emission measured with the scanning anode. The highest emission point is located at the edge of the deformed site, and from the SEM micrograph the edge is the most protruded and roughest place. The spot Auger measurement showed that Si, C, and SiC produced from the melting of DLC and Si were mixed together at the sites [9]. Since work functions of these materials are not so low to allow the drastic increase in the emission, we propose that the emission accompanied by the morphology change was due to the electric field enhancement through the surface roughening under the high bias voltage

and the arcing. Nitrogen doping will increase the bulk conductivity and increase the number of electrons to reach the surface for the emission, but unless the surface barrier for the emission into the vacuum is lowered the effect of the increased conductivity is limited. Since nitrogen doping does not lowered the work function and since the emission current from flat DLC film is usually small compared to the bulk conductivity, nitrogen doping effect is difficult to observe. Therefore, in the present study, the field enhancement due to the morphology change by arcing acts as a more important factor in the increased emission. We measured the electric field distribution using electric force microscope, and the result showed that there was a close correspondence between the surface roughness and the electric field [10].

IV. Conclusions

We deposited DLC films on Ti, ITO, and Si substrates for use as a thin film field emitter. We grew the films by sputtering a high purity graphite target with Ar ions. We made nitrogen-doped films by implanting nitrogen ions into the DLC film while the film was being grown. From the films we made, we were able to detect the measurable emission only after the breakdown occurred. The surface morphology after the breakdown was different for different substrates, and this was closely related to the stability of the emission. Using a high resolution scanning anode, we found that the emission was localized at the deformed sites created by the breakdown. The chemical and morphological analysis led to the conclusion that the formation of a stable material and the electric field enhancement through the surface roughening due to high bias voltage was responsible for the improved emission.

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