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Fabrication and field emission properties of poly-diamond films

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Abstract

By using a substrate transferring technique, poly-diamond thick films having a smooth or rough surface could be fabricated as field emitter materials. The diamond film with a smooth surface, which was transferred from the interface between the (100) Si substrate and poly-diamond deposited by plasma-enhanced CVD, showed better field emission properties in terms of emission current density with improved vacuum level dependence as compared with original poly-diamond film from a rough surface.

Keywords: Field emission; Diamond; Film

1. Introduction

Diamond-related materials such as single, polycrystalline diamond and diamond-like carbon (DLC) films have highly desirable properties as field emitter materials [1–6]. These films have low work function, good physical and chemical stability as well as strong mechanical hardness and high thermal conduction. Up to now, the emitting sites of diamond-related materials have not been determined definitely, although many studies assumed that the electrons might be emitted from either grain boundaries or peaks of the poly-diamond film. In this study, considering the emitting sites as both grain boundaries and peaks, we proposed the technique by which more grain boundaries and peaks could be generated on the emitting surface of poly-diamond film and discussed the emission properties of the poly-diamond films fabricated by the devised process.

2. Fabrication of poly-diamond film emitters

A substrate transferring technique [7], as shown in Fig. 1, was employed in order to fabricate two types of diamond film having different surface geometry. First, a pretreatment process was performed on an RCA-cleaned (100) Si substrate by dipping it into 1-grit diamond powder contained in 40 ml of acetone in an ultrasonic bath. After acetone re-cleaning and drying by N_2 blowing, 100-thick poly-diamond films were deposited on the Si substrate covered with diamond particles by microwave plasma-enhanced CVD. Hydrogen containing 2% CH_4 was used as a reactant gas and the substrate temperature, microwave power and vacuum level were set up as 950°C, 500 W and 90 torr, respectively. The deposited poly-diamond films have two kinds of surface, Surface-A as a real top surface and Surface-B as an interface between diamond film and Si substrate as shown in Fig. 1.

The poly-diamond field emitter with Surface-A as an emitting surface could be fabricated according to PATH A in Fig. 1. After deposition of poly-diamond on the Si substrate, the Si substrate was completely removed by dipping it into an HF + HNO_3 (1:1) solution. The thick poly-diamond film that remained was then attached to a tungsten plate by conductive epoxy. In the case of PATH B, the diamond-coated Si substrate was bonded with the tungsten plate followed by the Si removal process of PATH A. As a final step, both surfaces were treated in a H_2 plasma (1.5 kW, 40 torr, 30 min) in order to remove surface contaminants such as oxygen and tungsten particles.

3. Characterization and discussion

Fig. 2(a) and (b) shows the AES results for the poly-diamond surfaces before and after H_2 plasma treatment, respectively. Carbon, tungsten and oxygen peaks are detected on the surface before the H_2 plasma treatment of Fig. 2(a). The carbon peak is considered to originate from the diamond material itself, while the peaks for tungsten and

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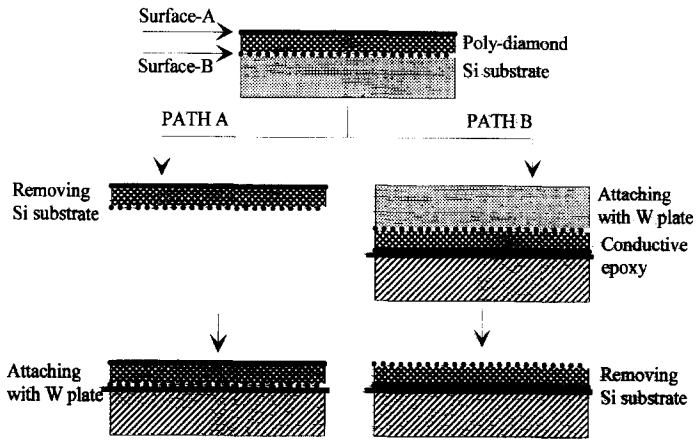

Fig. 1. Substrate transferring process of poly-diamond films.

oxygen contaminants might derive from the the tungsten plate and silica during the Si etching process in the HF + HNO_3 (1:1) solution. The contaminants might be a cause of change in work function and eventually, emission current fluctuations. These kinds of contaminants could be almost completely removed by a 30 min H_2 plasma treatment and the AES result following this is shown in Fig. 2(b).

Fig. 3 shows the Raman spectrum of the poly-diamond film. The first peak appears to be very sharp at 1332 cm^{-1} and the amorphous carbon peak near 1550 cm^{-1} is negligible indicating good crystalline property of the deposited poly-diamond film [8]. There were no differences in AES and Raman spectra for both cases of Surface-A and Surface-B.

SEM and AFM micrographs of the two types of fabricated poly-diamond films having Surface-A and Surface-B are shown in Fig. 4(a) and (b), respectively. It is known that Surface-A consists of large-sized grains ranging from a few to several tens of microns. The mean height and average roughness of Surface-A are found to be 2.94 μm and 0.86 μm, respectively. This kind of surface morphology is generally observed for the instance of poly-diamond films deposited by microwave plasma-enhanced CVD [9].

Also, Fig. 4(b) shows the SEM and AFM results of Surface-B obtained from the interface between the poly-diamond film and the (100) Si substrate. Only a few micron-sized grain boundaries are found on the surface in the SEM micrograph. It can be assumed that these micron-sized grains are generated as the diamond micro-crystals gradually grow from the initial nucleation step. The AFM measurement was carried out in an area of 3 × 3 μm^2, which was the area approximately equivalent to the size of one grain and a great number of micro-peaks were revealed on the surface. These have average height and roughness of about 230 Å and 51 Å, respectively. It can be inferred that the micro-peaks on the grain surface result from transient layers, like SiC, carbon or Si-related contaminants arising from etch-out during the wet chemical etching of the Si substrate and and subsequent H_2 plasma surface treatments.

Field emission properties were evaluated for the fabricated poly-diamond film emitters having the two types of surface geometries. Samples were prepared having emitting areas of 0.5 × 0.5 cm^2 and the vacuum level of the test chamber was maintained at 2 × 10^{-6} torr. A tungsten plate and polyimide film were employed as anode and spacer, respectively, and the emitter-to-anode distance was fixed to 50 μm. This measurement set-up was described previously [5].

The measured emission current–applied voltage curves are shown in Fig. 5(a). Although the turn-on electric field is about 15 V μm^{-1} for both Surface-A and Surface-B, relatively sharper and higher current curves were obtained from the poly-diamond emitters having a Surface-B. The emission current density at an applied field of 22 V μm^{-1} appeared to be 22 μA cm^{-2} and 800 μA cm^{-2} for Surface-A and Surface-B, respectively. From the Fowler–Nordheim plot shown in Fig. 5(b), it is evident that the emission current from Surface-B is closer to a traditional field emission current than the current from Surface-A. The increased number of peaks and grain boundaries (valleys) formed on Surface B of the poly-diamond film might be regarded as an indication of increased emission current density.

Fig. 6 shows the dependence of I–V characteristics upon the vacuum level of 10^{-4}, 10^{-5} and 10^{-6} torr for the

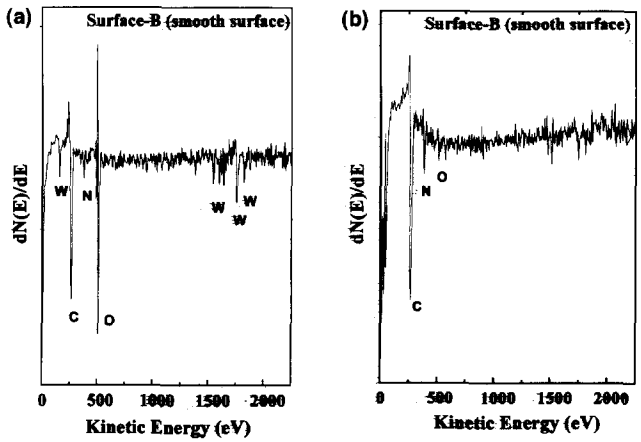

Fig. 2. AES results of diamond film surfaces (a) before, and (b) after H_2 plasma treatment.

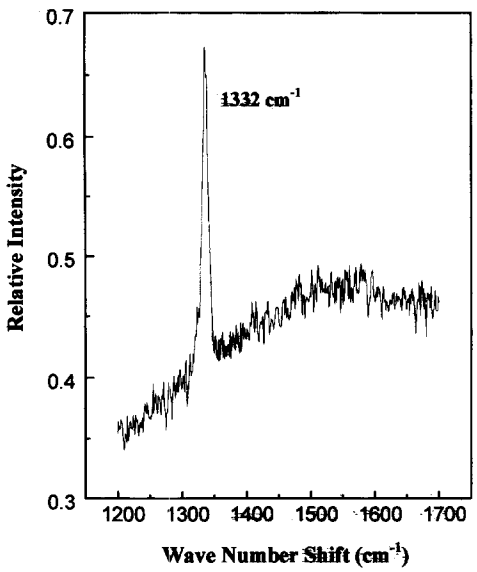

Fig. 3. Raman spectrum of the poly-diamond film deposited by microwave plasma-enhanced CVD.

poly-diamond film field emitters. In the case of a field emitter having a Surface-A, the field emission did not occur under 10^{-4} torr. However, field emission was observed at 10^{-4} Torr and the dependence of emission current on vacuum level was negligible in the vacuum level range of 10^{-6}–10^{-4} torr in the case of Surface-B, as shown in Fig. 6(b).

Two reasons can be suggested for Surface-B having a higher emission current and more stable operation at low vacuum as compared with Surface-A. First, the emitting sites (peaks and valleys) are dispersed non-uniformly and so the electrical turn-on might occurred randomly under an unstable mode for a rough surface like that of Surface-A. Additionally, the emission current generated from one emitting site (peaks or valleys) on Surface-A must be increased in order to keep the same emission current level as that from Surface-B on which there are a more uniform and larger number of emitting sites. The high current might cause an undesirable reaction with ambient gases and degradation of the emitting sites which finally collapse under a low vacuum level of 10^{-4} torr.

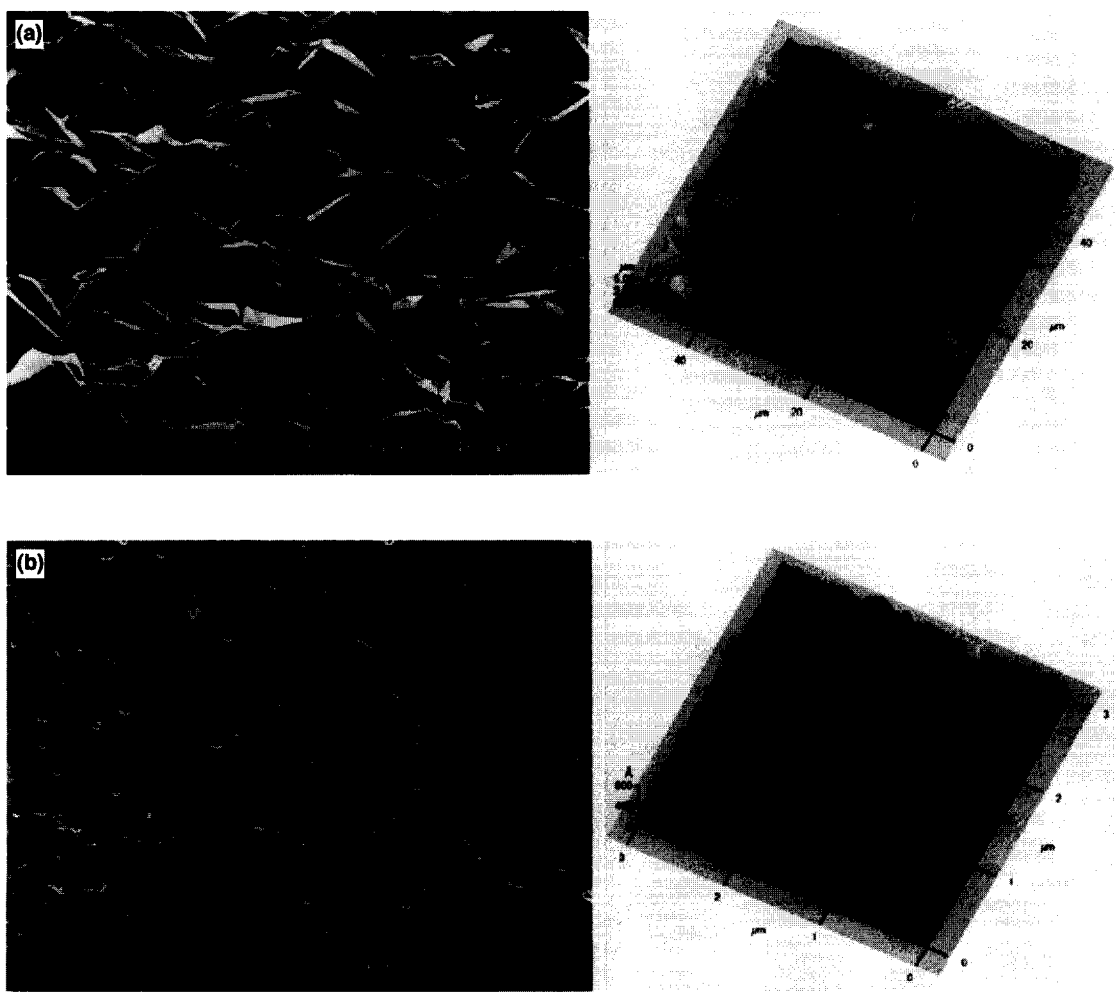

Fig. 4. SEM and AFM data of the two types of surfaces. (a) Surface-A (rough surface); (b) Surface-B (smooth surface).

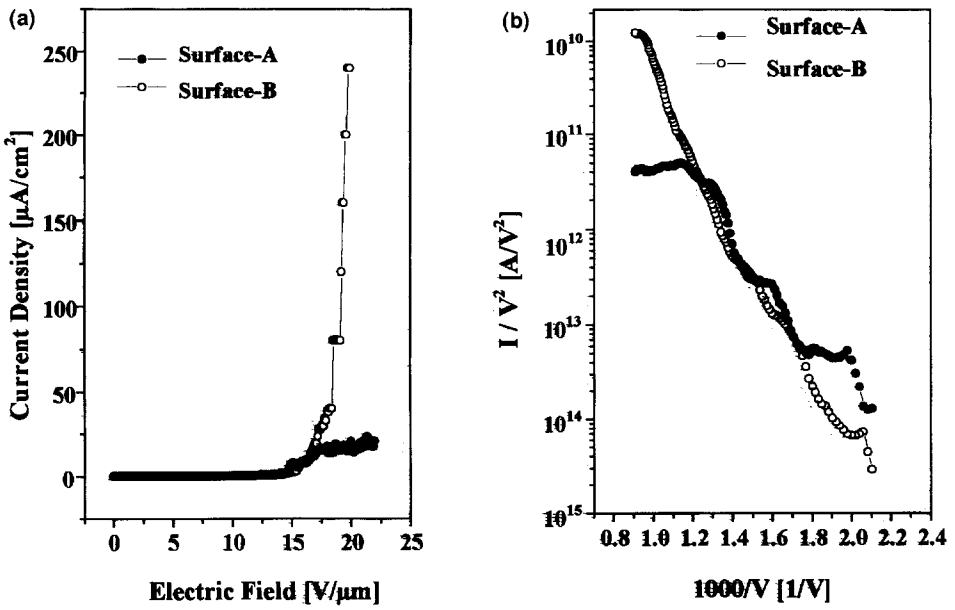

Fig. 5. Field emission characteristics of the fabricated poly-diamond field emitters. (a) I–V curve; (b) Fowler–Nordheim plot.

4. Conclusion

A poly-diamond surface having a high density of peaks and valleys could be fabricated by a substrate transferring technique. The fabricated poly-diamond film emitter with a smooth surface and a large number of emitting sites showed improved field emission properties in terms of emission current and vacuum-level dependence as compared with those field emmission properties from the conventional poly-diamond film. The increased number of emitting sites and the improved geometrical uniformity might be major factors contributing to the increased emission current density and stability.

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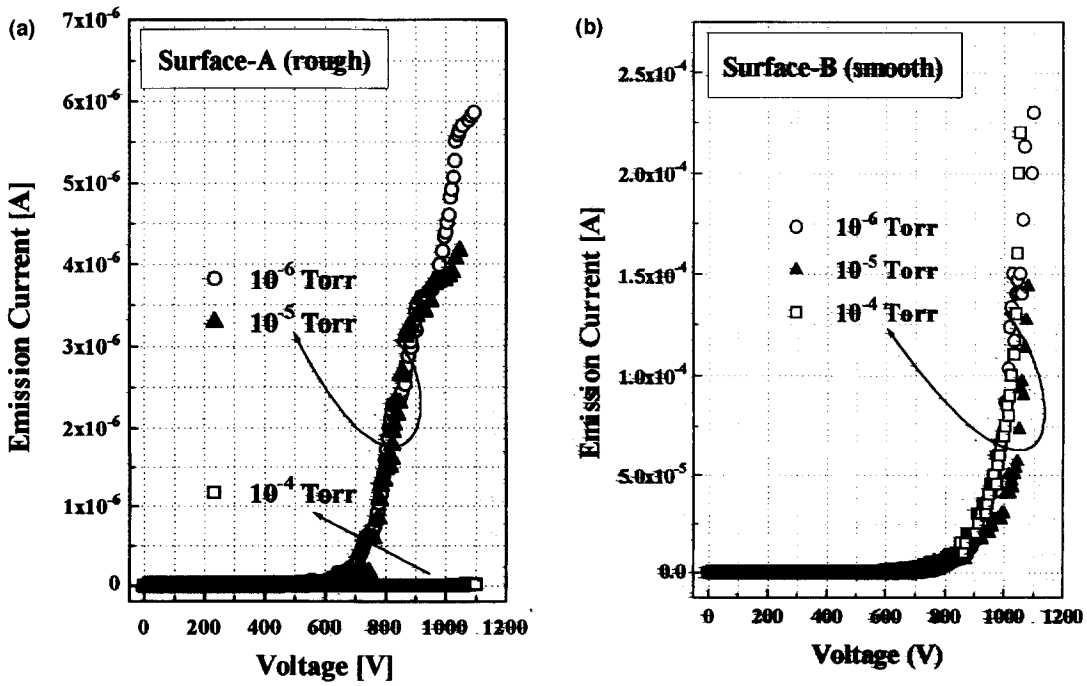

Fig. 6. Dependence of field emission characteristics on vacuum level. (a) Surface-A; (b) Surface-B.

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