Composite diamond-like carbon and silicon carbide tips grown on oblique-cut Si(111) substrates

W. Y. Yeh and J. Hwang[a)]
Department of Materials Science and Engineering, National Tsing Hua University, Hsin-Chu City, Taiwan, Republic of China

A. P. Lee and C. S. Kou
Department of Physics, National Tsing Hua University, Hsin-Chu City, Taiwan, Republic of China

H. Chang
Department of Chemistry, National Tsing Hua University, Hsin-Chu City, Taiwan, Republic of China

(Received 13 March 2001; accepted for publication 2 October 2001)

A diamond-like carbon (DLC) and silicon carbide (SiC) composite tip structure was successfully deposited on an oblique-cut Si(111) substrate of terrace width less than 21.1 Å. The DLC morphology depended on the Si(111) terrace width in the oblique-cut Si(111) surface. A continuous and dense DLC film started to form on the Si(111) substrate of terrace width higher than 27.8 Å. The density of the DLC/SiC composite tip also depended on the terrace width. The DLC films on the Si(111) with or without oblique cut had about the same Raman characteristics regardless of their different morphologies. The formation mechanism of the DLC/SiC tip structure was discussed. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1421427]

The microfabricated field emitter has been an active research topic in the field of cold-cathode field-emission displays.[1–4] Sharp tip shape and low work function, which enhance emission current at low electric field, are two major characteristics of an excellent field emitter. Carbon nanotubes have excellent field-emission properties mainly due to their sharp tube structures.[5,6] Low-voltage field emission has also been observed in microfabricated flat cathodes coated with diamond-based or diamond-like carbon (DLC) films.[7,8] The lack of sharp tip structure of the DLC-coated cathode has still attracted much attention based on the following reasons. First, the deposition of DLC film is a low-temperature and low-cost process. Second, uniform DLC films of large area are easier to deposit on Si than nanotubes or diamond-based films. Third, the DLC films also have excellent field-emission properties. The applied electric field can be lowered to 3 V/μm while the field-emission current is in the μA range.[1] In the past few years, the research direction on the DLC field emitter has been to improve field-emission performance by controlling the sp^2 cluster size,[3] the thickness of the DLC film,[9] nitrogen content in the DLC film,[10] or changing the synthesis method.[11] In this letter, we will present an approach to deposit a composite tip structure of DLC and silicon carbide (SiC) on oblique-cut Si(111) substrates, which may open a sight to fabricating a DLC-based field emitter.

Oblique-cut Si(111) wafers were prepared by tilting the silicon rod from [111] toward the [11$\bar{2}$] direction during slicing. Different tilt angles α were chosen in order to obtain different terrace widths on the oblique-cut Si(111) surface. Terrace width is a representation of the number of atomic rows in the Si(111) terrace parallel to the ledge. The narrower the terrace width, the more ledge sites. The corresponding terrace widths and the number of atomic rows for the oblique-cut Si(111) samples are listed in Table I. The oblique-cut Si(111) substrates were cleaned with acetone and deionized water and then put into a planar microwave plasma-enhanced chemical-vapor deposition system.[12] The chamber was first pumped to a base pressure of 5×10^{-3} Torr, and H_2 and CH_4 was then fed into the chamber to ignite the CH_4/H_2 mixed plasma operated at 3000 W. DLC films were deposited on the oblique-cut Si(111) substrates at 200 °C and 0.18 Torr pressure through a two-step biased process. At the first step, the substrate was biased at −250 V and the CH_4/H_2 ratio was kept at 2% for a deposition period of 0.5 h. The CH_4/H_2 ratio was then switched to 30% for a deposition period of 3.5 h at the second step. The morphologies of the deposited samples were characterized by using a JSM-6330F field-emission scanning electron microscope (FESEM) in cross-sectional view. The deposited samples were cleaved along the Si[110] direction in air before FESEM observation. The chemical information of the deposited samples was characterized by using PHI 670xi Auger electron spectroscopy (AES) and Raman spectroscopy excited by 514.5 nm Ar laser radiation.

Figures 1(a), 1(b), 1(c), and 1(d) show the cross-sectional FESEM micrographs of the cleaved DLC films grown on the oblique-cut Si(111) substrates of different terrace widths. A smooth and dense DLC film without pinholes

TABLE I. Corresponding terrace width and the number of atomic rows parallel to the ledge in the terrace for the oblique-cut Si(111) samples.

α angle (°)	Terrace width (Å)	Number of atomic rows
0	Infinite	Infinite
6.45	27.8	8
8.47	21.1	6
12.27	14.4	4

[a)]Electronic mail: jch@mse.nthu.edu.tw

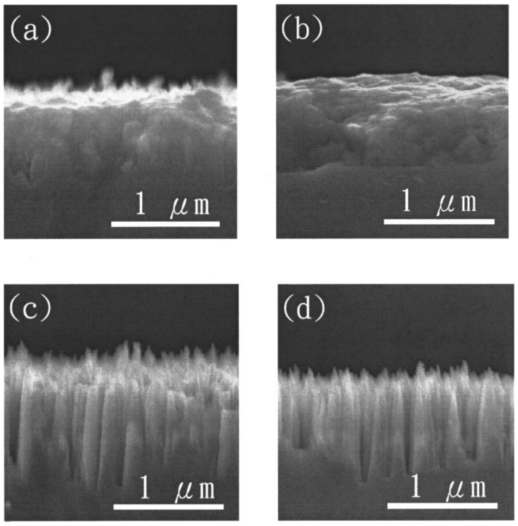

FIG. 1. Cross-sectional FESEM micrographs of cleaved DLC films deposited on different oblique-cut Si(111) substrates. Corresponding Si(111) terrace widths are (a) infinite, (b) 27.8 Å, (c) 21.1 Å, and (d) 14.4 Å.

appears on the Si(111) surface without the oblique cut. When the Si(111) terrace width reduces to 27.8 Å, the morphology of the DLC film remains about the same in most surface areas, as shown in Fig. 1(b). A DLC tip structure, however, appears in some surface areas. The Si substrate is completely covered with the DLC tip structure when the Si(111) terrace width reduces further to 21.1 and 14.4 Å, as shown in Figs. 1(c) and 1(d), respectively. All the DLC tips have about the same length of approximately 1 μm, but the tip density increases with reducing the Si(111) terrace width. The tip density is estimated to be 25 and 38 μm^{-2}, respectively, for the Si(111) terrace widths of 21.1 and 14.4 Å. The DLC tips form an irregular interface with the Si substrate, which is unlike the DLC/Si interface in Fig. 1(a) or 1(b). The irregular interface is considered not to be the original Si surface since it is much more rough than what a polished Si(111) surface should be.

In order to clarify the reaction that occurred at the interface, Si and C Auger line scans have been performed across a tip in Fig. 1(c). Figure 2(a) shows the Si and C concentration profiles along the straight line across Si and the tip. The Auger signals are noisy since the electron beam of the PHI 670xi AES system was operated at 20 kV and 1 nA in order to obtain an *in situ* FESEM image good enough to locate the scan line along the tip. The Si signal stays roughly at the same magnitude inside the Si substrate and drops to a lower magnitude at the bottom part of the tip, and then further decreases down to a noise level at the end of the tip. In contrast, the C signal reaches a maximum value around the end of the tip, and drops to a constant value at the bottom part of the tip, and then decreases to a noise level inside the Si substrate. Note that the Si signal reaches along the tip at a position about 0.5 μm away from the irregular interface. This suggests Si atoms diffusing out of the Si substrate toward the end of the tip, rather than carbon diffusing into the Si substrate. Based on the noisy Si/C signal ratio, the scanned area can be roughly divided into the three ''Si-rich,'' ''SiC,'' and ''C-rich'' regions, as marked in Fig. 2(b). The SiC region may be considered to be the SiC phase based on two reasons. First, a SiC interlayer has been very often ob-

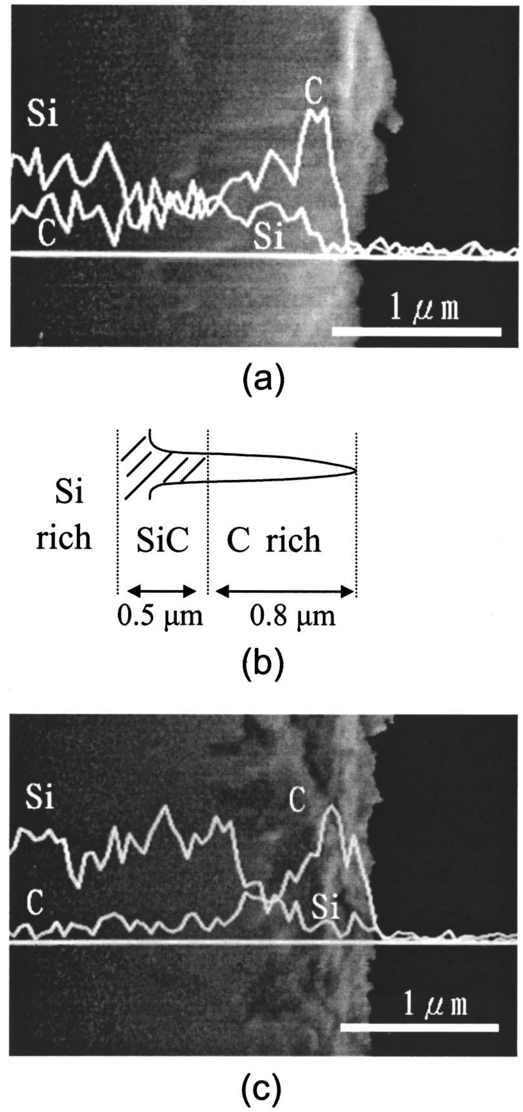

FIG. 2. (a) Si and C Auger concentration profiles along a tip on oblique-cut Si(111) of 21.1 Å terrace width, (b) sketch showing three regions along the tip in (a), and (c) Si and C Auger concentration profiles along the scan line across the DLC film deposited on Si(111).

served at the interface between the carbon-based film and the Si substrate.[13,14] Second, both Si and C Auger signals stay about the same in the SiC region, as shown in Fig. 2(a). The C-rich region was determined to be a DLC film,[15] which is evident by the two broad Raman peaks centered at about 1340 and 1600 cm^{-1}. The irregular interface between Si and the tip is obviously the interface between the Si-rich and SiC regions, as shown in Fig. 2(a). Therefore, the tip is a DLC/SiC composite structure consisting of about 0.5-μm-long SiC at its bottom part and 0.8-μm-long DLC at its upper part.

Auger line scans and Raman measurements have also been performed on a continuous and dense films, as shown in Fig. 1(a). The Si Auger signal stays at about the same magnitude inside the Si substrate and rapidly decreases down to a noise level at the top of the film, as shown in Fig. 2(c). In contrast, the C Auger signal reaches a maximum value around the top of the film, and decreases to a noise level inside the Si substrate. The Si and C Auger signals suggest the existence of Si- and C-rich regions. The C rich was determined to be a DLC film[15] since two broad Raman peaks centered at about 1340 and 1600 cm^{-1} were also observed. There is no finite region of the Si/C ratio roughly equal to 1. The SiC region in the DLC/SiC composite tip structure is no longer observed inside the continuous and dense film.

The formation of the DLC/SiC composite tip is proposed and described below. At the beginning of the diamond-like carbon deposition onto the oblique-cut Si(111) surface, C-containing radicals start to react with Si and form a SiC layer at the top. With enough supply of Si atoms toward the top of the SiC layer, the SiC layer continues to form and grows thicker. The SiC thickness in the DLC/SiC composite tip, approximately 0.5 μm, is much larger than that previously reported at the DLC/Si interface.[14] The SiC formation is enhanced especially on the oblique-cut Si(111) surface of smaller terrace width, since the Si atom is less bonded at the kink sites and the ledge sites. SiC spikes form on the SiC surface as the Si(111) terrace width is less than or equal to 21.1 Å. The formation mechanism of SiC spikes is unclear now. This may be due to the local inhomogeneous C-containing radical concentration on the SiC surface that very probably results from the fast SiC reaction. Finally, DLC tips form at the top of the SiC spikes based on the following reasons. First, C deposition is enhanced locally at the spike position on the SiC surface due to the higher electric-field effect since the substrate is biased with −250 V during deposition. As the DLC tips grow further, the electric-field effect is enhanced more at the tip position that may result in the formation of the DLC tip structure on the SiC surface.

In summary, a DLC/SiC composite tip structure has been successfully grown on an oblique-cut Si(111) surface of terrace width less than 21.1 Å. The critical Si(111) terrace width is around 21.1 Å, beyond that a continuous and dense DLC film starts to appear. The concept of terrace width opens an approach in the control of the morphology of DLC film on Si substrates. The DLC/SiC composite tip may be useful as a field emitter due to its sharp structure.

This work is supported by the National Science Council, R.O.C. through Project No. NSC 89-2218-E-007-009.

[1] O. Gröning, O. M. Küttel, P. Gröning, and L. Schlapbach, Appl. Phys. Lett. **71**, 2253 (1997).
[2] O. Gröning, O. M. Küttel, P. Gröning, and L. Schlapbach, Appl. Surf. Sci. **111**, 135 (1997).
[3] A. llie, A. C. Ferrari, T. Yagi, and J. Robertson, Appl. Phys. Lett. **76**, 2627 (2000).
[4] J. D. Carey, R. D. Forrest, R. U. A. Khan, and S. R. P. Silva, Appl. Phys. Lett. **77**, 2006 (2000).
[5] Y. Chen, D. T. Shaw, and L. Guo, Appl. Phys. Lett. **76**, 2469 (2000).
[6] J. l. Sohn, S. Lee, Y.-H. Song, S.-Y. Choi, K.-l. Cho, and K.-S. Nam, Appl. Phys. Lett. **78**, 901 (2001).
[7] K. Okano, S. Koizumi, S. Ravi, P. Silva, and G. A. J. Amaratunga, Nature (London) **381**, 140 (1996).
[8] D. S. Mao, J. Zhao, W. Li, C. X. Ren, X. Wang, X. H. Liu, J. Y. Zhou, Z. Fan, Y. K. Zhu, Q. Li, and J. F. Xu, J. Vac. Sci. Technol. B **17**, 311 (1999).
[9] R. D. Forrest, A. P. Burden, S. R. P. Silva, L. K. Cheah, and X. Shi, Appl. Phys. Lett. **73**, 3784 (1998).
[10] K.-R. Lee, K. Y. Eun, S. Lee, and D.-R. Jeon, Thin Solid Films **290-291**, 171 (1996).
[11] R. Wächter, A. Cordery, S. Proffitt, and J. S. Foord, Diamond Relat. Mater. **7**, 687 (1998).
[12] T. J. Wu and C. S. Kou, Rev. Sci. Instrum. **70**, 2331 (1999).
[13] D. B. Dimitrov, D. Papadimitriou, and G. Beshkov, Diamond Relat. Mater. **8**, 1148 (1999).
[14] D. N. Belton, S. J. Harris, S. J. Schmieg, A. M. Weiner, and T. A. Perry, Appl. Phys. Lett. **54**, 416 (1989).
[15] K. E. Spear and J. P. Dismukes, in *Synthetic Diamond: Emerging CVD Science and Technology* (Wiley, New York, 1994), pp. 114 and 115.