Effect of Surface Structure of Sapphire A-Face on Directional Carbon Nanotube Growth

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The surface structure change of sapphire A-face (1 1 −2 0) by heating in air has been investigated from the point of view of its influence on the aligned growth of single wall carbon nanotubes (SWCNTs). The step shape was getting regular with an increase of the annealing temperature, and straight step array appeared at 1473 K. A further increase of the temperature to 1523 K resulted in altered region formation on terraces, although the atomic step shape was not changed. A terrace appeared as if it had been divided into two sub-terraces, but the height difference was less than 0.1 nm. Secondary electron images showed different contrasts in two regions, suggesting a compositional difference between them. Aligned SWCNTs were obtained regardless of the annealing temperature up to 1473 K. However, on the 1523 K-annealed surface, SWCNTs grew irregularly. The altered region changed the interaction between SWCNTs and the surface. [DOI: 10.1380/ejssnt.2009.904]

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I. INTRODUCTION

Aligned growth of single wall carbon nanotubes (SWCNTs) has been found on sapphire (1 1 −2 0) (A-face) and (1 −1 0 2) (R-face) surfaces [1–4]. This is a directional growth along specific crystal orientations on these surfaces. This phenomenon is useful for device applications, but the mechanism of alignment is not clear. A small anisotropy of molecular force between the surface atom rows and a SWCNT seems to be an only reasonable explanation of the phenomenon. Investigation of the effect of surface modification on the SWCNT alignment as well as that of other material surfaces is desirable for the elucidation of the alignment mechanism. From this viewpoint, well-defined sapphire surfaces are necessary to study the interaction with SWCNTs. Actually, the atomic scale surface morphology depends on the treatment of the substrate and crystal face. Yoshihito et al. first reported atomic scale smoothening of the sapphire surface by air-heating [5]. After that, many papers on surface morphology of annealed sapphire surfaces have been reported [6–12]. Most papers concern (0 0 0 1) (C-face) surfaces, which are widely used for the epitaxial substrates of nitride semiconductors, diamond, etc. There are not many studies on A- and R-faces. Nguyen et al. examined R-face annealed at 1023-1353 K and reported highly-irregular zigzag atomic steps caused by anisotropic surface diffusion [11]. Simeonov and Lederman studied the morphology of A-face annealed at 1373-1873 K, and reported bunching of steps and faceting of step edges [12]. These studies show that the atomic step shapes on A- and R-faces strongly depend on the annealing temperature, as well as the step orientation.

In this paper, we investigated the step morphology and a possible compositional change of sapphire A-face by high temperature heating in air. SWCNTs were grown on the surface-modified substrates and directionality of SWCNT extension was examined.

II. EXPERIMENTAL

The sapphire substrate used had an A-face with a small miscut angle of < 0.1° (Namiki, Tokyo, Japan). Because of the small miscut angle, the step direction and spacing changed locally depending on the waviness of the substrate surface. The substrate was annealed at 1273-1523 K in air for 3-5 hours. SWCNT growth was performed by chemical vapor deposition (CVD) with Fe as the catalyst and ethanol as the source gas. The Fe catalyst was prepared by depositing sub-monolayer Fe with nominal thickness of 0.02 nm in a vacuum evaporator. Before the CVD process, the sample was annealed at 1123 K for 5 min in 300 sccm Ar/H₂ (3% by volume) at 9.3×10⁴ Pa. Keeping the temperature at 1123 K, ethanol vapor was introduced to start CVD growth by babbling through liquid ethanol with the Ar/H₂ gas of 25 sccm. The growth duration was 5 min. The surface morphology and SWCNTs were observed by scanning electron microscopy (SEM) at a low acceleration voltage (0.5 kV) and atomic force microscopy (AFM).

III. RESULTS AND DISCUSSION

AFM images for as-received and 1273-1473 K-annealed substrates are shown in Fig. 1. The arrows indicate the [1 −1 0 0] direction. Since the sapphire wafer with surface waviness was cut into small pieces (10-20 mm²) and each one was annealed at different temperature, the step directions were not the same for all the substrates. The as-received surface (Fig. 1(a)) has a step-terrace structure, but the step edges are rough. The step edges of the 1273 K-annealed surface are still rough, but elongated grooves along the [1 −1 0 0] direction are seen on the terraces (Fig. 1(b)). These grooves are almost parallel to the step edge. The grooves on the terrace disappear and the step edges are continuous on the 1373 K-annealed surface.
FIG. 1: AFM images of A-face sapphire substrates (a) without annealing, (b) with annealing at 1273 K, (c) with annealing at 1373 K, and (d) with annealing at 1473 K. Arrows indicate the [1\(-1\) 0 0] direction.

(Fig. 1(c)). On this sample surface, the step direction is almost perpendicular to the [1\(-1\) 0 0] direction. Thus, the steps have peninsula-like shapes along the [1\(-1\) 0 0] direction. After 1475 K annealing, the step edges become straighter (Fig. 1(d)).

After annealing at 1523 K in air, the surface exhibits a new feature as shown in Fig. 2. In the SEM image (Fig. 2(a)), two different contrast regions are seen. Their boundaries can be observed on the terraces in the AFM image (Fig. 2(b)). One corresponds to the step edge and the other is located in the middle of the terrace. As shown in Fig. 2(c), the height difference between the two regions on the terrace is less than 0.1 nm, which is smaller than the monolayer-step height (0.216 nm) on the A-face. While the step edges are straighter, the boundary of the two regions on the terrace is rougher. Comparing the SEM and AFM images, the brighter regions in the SEM image correspond to the upper region of a monolayer step.

The step-terrace structure of sapphire R-face (1\(-1\) 1 0 2) has been reported to change during air heating. Elongated 2-dimensional islands along the [\(-1\) \(1\) 1 0] direction were observed and attributed to anisotropic surface diffusion along the surface atomic row [11]. The present elongated groove or peninsula structures along the [1\(-1\) 0 0] direction on the A-face can also be interpreted as the anisotropic surface diffusion.

However, a double-region structure has not previously been reported on the R-face or A-face. In the present study, the temperature difference of 50 K caused the double-region formation. The critical temperature would depend on the terrace width, and a higher temperature would be needed for narrower terraces. Also, the height difference of the boundary on the terrace is so small that it is not easy to recognize the double-region structure only by AFM. On the other hand, the double-region structure
FIG. 3: SEM images of SWCNTs grown on A-face sapphire substrates (a) without annealing, (b) with pre-annealing at 1273 K, (c) with pre-annealing at 1373 K, and (d) with pre-annealing at 1523 K. Arrows indicate the $[1\ -1\ 0\ 0]$ direction.

is clearly seen in the SEM image. The origin of contrast change in the SEM image could be changes in surface roughness, composition or crystallinity (order vs. disorder). Since the AFM image shows no distinct difference of surface roughness between the two regions, composition or crystallinity change is plausible. The origin will be discussed later. Hereafter, we call the bright contrast region as “altered region”.

SWCNTs were grown on the series of the substrates with different annealing temperatures. SEM images of the SWCNT grown substrates are shown in Fig. 3. On the as received substrate and 1273-1373 K-annealed substrates, SWCNT are straight and well aligned along the $[1\ -1\ 0\ 0]$ direction (Figs. 3(a)-3(c)). In contrast, SWCNTs become randomly oriented and the straightness obviously degrades on the 1523 K-annealed substrate. While the step morphology and the terrace roughness changed drastically by the air heating at 1273-1473 K, the directional growth of SWCNT was hardly affected by the step morphology change.

To elucidate the cause of the disorder on the 1523 K-annealed substrate, a lower density of SWCNTs was grown and observed by SEM and AFM. As shown in Fig. 4(a), the double-region structure can be still observed by SEM after SWCNT growth. Interestingly, Fe catalyst particles are selectively formed on the bright contrast regions in the SEM image, i.e. on the altered regions. This is confirmed by the AFM image shown in Fig. 4(b). Some SWCNTs are aligned along the $[1\ -1\ 0\ 0]$ direction, but most SWCNTs extend in random directions starting from the altered regions.

The 1523 K-annealed substrate had a nonuniform distribution of the altered regions. By using the nonuniformity, SWCNT growth behavior on a narrow altered area was examined. As shown in Fig. 5, catalyst particles are confined on the altered regions, and all the SWCNTs contact the catalyst regions. Some long SWCNTs are aligned along the $[1\ -1\ 0\ 0]$ direction. These results suggest that SWCNTs initially extend in random directions when nucleated from the altered regions, and they can be aligned along the $[1\ -1\ 0\ 0]$ direction when extending on the non-altered regions. When the area of the altered layer is large, such as the image shown in Fig. 4, SWCNTs are hardly aligned along the $[1\ -1\ 0\ 0]$ direction.

FIG. 4: (a) SEM and (b) AFM images of SWCNTs grown on A-face sapphire substrate with pre-annealing at 1523 K. Arrows indicate the $[1\ -1\ 0\ 0]$ direction.

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FIG. 5: SEM images of SWCNTs grown on A-face sapphire substrate observed at (a) wide altered region and (b) narrow altered region. Arrows indicate the $[1 − 1 0 0]$ direction.

The above results show that the altered region greatly affects the SWCNT growth. Probably, the topmost surface atomic arrangement is different from that on the normal A-face. Since the altered region forms from the top edge of an atomic step, oxygen or aluminum atoms evaporate from the step edge. Considering the facts that oxidation atmosphere at a high temperature is necessary for the regular step-terrace structure on the sapphire surface, and a very high temperature causes the altered region formation, oxygen atoms play an important role on the surface. Oxygen deficiency likely takes place at the high temperature. This is consistent with the higher secondary electron yield of the altered region. Because oxygen is an electronegative element, oxygen deficiency at the topmost surface causes the enhancement of electric dipole toward vacuum from the surface. This lowers the work function, leading a higher secondary electron yield. In addition, oxygen deficiency also causes an increase of dangling bond density, which can explain the reduced surface diffusion, and the selective nucleation of Fe particles. It has been shown that higher density and smaller catalyst (Co or Fe) particles are formed on the amorphous $\gamma$-alumina surface [13]. The topmost surface of the altered region may be compared to the amorphous $\gamma$-alumina surface.

It should be noted that the altered region is limited to the topmost layer. A transmission electron microscopy observation of a thinned sample did not show any contrast corresponding to the double-region structure. Nor an X-ray photoelectron spectroscopy measurement at a large take-off angle detected any change in the surface composition on the double-region structure. The change is smaller than the detection limits of these measurements. Nevertheless, the altered region greatly affects the nanotube growth. In this sense, SWCNTs are quite sensitive to atomic arrangement of the topmost surface, while they are insensitive to surface roughness.

IV. CONCLUSIONS

We have found altered regions are formed in the upper terrace near the step edge on sapphire A-face by air-heating at as high as 1523 K. The altered region exhibited brighter contrast in an SEM image, thus a stripe image was observed. Fe nanoparticles were selectively formed on the altered region, revealing a reduced surface diffusion on it. SWCNTs, which normally grow along the $[1 − 1 0 0]$ direction on the sapphire A-face, were randomly oriented on the altered region. The altered region likely has oxygen deficiency at the topmost layer caused by the high temperature annealing.

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