THE EFFECT OF BOTTOM ALIGNMENT OF CARBON NANOTUBE FOREST ON ITS SPINNABILITY

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1 Introduction

Despite their excellent strength and thermal and electrical conductivity, the application of carbon nanotubes has largely been limited due to its shortness. Yarning carbon nanotubes (CNTs) into long fiber has the potential to realize CNT's unique properties at the macro-scale world [1]. CNT forests that can be directly spun into pure yarn are called 'spinnable' forests and widely researched by many groups [2-5]. They have inherent advantages in conductivities over other spinning methods that contain impurities [2]. The conditions to produce spinnable CNT forests are extremely sensitive, so many researchers have tried to elucidate the factors for spinnablilty [6, 7]. The fact that the forests should be highly aligned in order to be spun is now generally known [6-8]. However, the effect of the alignment at the bottom part on spinnability has been quite controversial [6, 9]. Here, we demonstrate the effect of the alignment at the bottom part on spinnability by controlling the alignment at the bottom part and comparing the spinnability of each case.

2 Experiment

We used a radio frequency plasma enhanced chemical vapor deposition (rf-PECVD) reactor to synthesize CNT forest. On a Si wafer, 10 nm of Al_2O_3 layer was deposited through atomic layer deposition and, as a catalyst, 1 nm of Fe layer was coated by e-beam evaporation on it. The wafer was loaded inside the reactor and the reactor was evacuated. The reactor was heated to 730 ℃ in 4 min with flowing Ar gas. The gaseous mixture of Ar, H_2, and C_2H_2 was introduced and the synthesis was carried out with 800 W of plasma and 300 W of bias plasma for 15 min. The reaction was terminated by shutting off C_2H_2 gas supply and turning off the heater. We tried two different termination modes named 'blowing-off' process and 'normal' process, respectively. In the blowing-off process, when terminating the reaction, excessive amount of Ar and H_2 gas was introduced to blow off the residual carbon species instantaneously and in the normal process, the same flow rate of Ar as in the reaction was maintained.

To further generalize the result, the synthesis was also taken through a chemical vapor deposition method where plasma was not generated. The same catalyst was inserted in a tube reactor and the reactor was heated to above 700 °C in 25 min with flowing Ar gas. The synthesis was run for 10 min and terminated by the two same methods, blowing-off process and normal process, used in the synthesis using PECVD. In both the experiments, the samples were taken out after being cooled down to below 200 ℃. As-obtained CNT forests were directly pulled away using a pair of tweezers to assess the spinnability

3 Results and discussion

As shown in fig. 1 (a) and (b), the CNT forests were successfully synthesized with excellent vertical alignment. This good alignment is attributed to the bias plasma effect. Bias plasma may lead to unidirectional growth of CNTs. However, we found two different kinds of samples in its morphology at their root regions. One is disordered and poorly aligned as shown in fig. 1 (b) while the other is well aligned to the bottom as shown in fig. 1 (d).

This different geometry at the root region may result from the root growth mechanism. Depending on the growth point, there are two kinds of growth mechanisms, they are, root growth and tip growth.

The synthesis of CNT forests in our system is believed to be root growth mode, as observed by other groups, due to good interaction between Fe nano-particles and Al_2O_3 buffer layer [8-10]. Based on their root growth property, we thought that the alignment of CNTs at the bottom region is determined at the end of the synthesis.
When we terminate the synthesis by the normal process, the C_2H_2 gas is still present for some time after shutting off the gas supply, and temperature is still high after turning off the heater. Therefore, there exists enough chance for the remaining C_2H_2 gas to be decomposed on the catalyst in a condition which is far from the optimum condition for the synthesis of super-aligned CNT forests in terms of gas composition, temperature, gas flow, pressure, etc. This leads to the poor alignment at the bottom region of the CNT forest as Fig. 1 (b). To the contrary, when we terminate the synthesis by the blowing-off process, the residual C_2H_2 gas is completely removed from the substrate right after shutting off the C_2H_2 supply. Thus, the growth of CNTs stops immediately and the poor alignment at the bottom region does not occur.

We focused on the effect of this different morphology at the bottom region on spinnability. Each sample was tested its spinnability after the growth. There was a clear difference between two samples. CNT forest with poor alignment at the bottom region was not spinnable even though it had good alignment as a whole. To the contrary, the CNT forest with good alignment at the bottom region was continuously spinnable. This means that the disordered region badly affects the spinning process.
Figure 2 displays the direct yarning process. When a CNT forest was directly pulled away using a pair of tweezers, a CNT yarn was continuously spun. The length of the obtained CNT yarn was 75 cm. Fig. 3 shows SEM images for the CNT yarn directly spun from CNT forest.
To further verify the effect of the alignment at the root region of CNT forest on its spinnability, we carried out the same experiments using thermal CVD. By adjusting experimental parameters, we could also synthesize CNT forest with good alignment in the absence of plasma. The two different reaction termination processes were also employed and the same phenomenon was observed. With the blowing-off process, we could obtain the well-aligned root region, but with the normal process, we could observe poor alignment at the root region, as displayed in fig. 4 (a) and (b) respectively.
The CNT forests grown by thermal CVD process were also tested their spinnability. Also in this case, the CNT forest with well-ordered bottom region was spinnable while the other was not spinnable. This is consistent with the fact that the alignment at the bottom region of the CNT forest is important for spinnability as observed in the CNT forests grown by PECVD process.

4 Conclusion

We synthesized well-aligned CNT forests on a Si wafer through PECVD process. We observed two types of CNT forests having different bottom alignments and revealed that this is because the different reaction termination process. Due to its bottom growth property, the residual C_2H_2 gas after shutting off the C_2H_2 supply results in poor alignment at the bottom region. In the blowing-off process, the residual C_2H_2 gas is quickly removed, resulting good alignment throughout the CNT forest. We tested the effect of this different geometry of the root region of CNT forest on its spinnability. We conclude that the one with well-aligned bottom morphology is easily spinnable while poorly-aligned one is not spinnable. To further generalize the result, the same experiment was carried out using thermal CVD. Both the results from PECVD and thermal CVD processes were consistent with each other. We obtained a CNT yarn whose length reaches 75 cm.

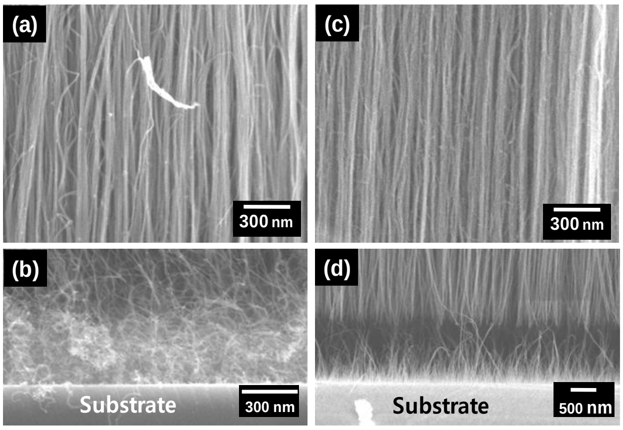

Fig. 1. Scanning Electron Micrograph (SEM) images of CNT forests obtained through different reaction terminating processes. The upper (a) and root (b) region from the 'normal' terminating process and the upper (c) and root (d) region from the 'blowing-off' process.

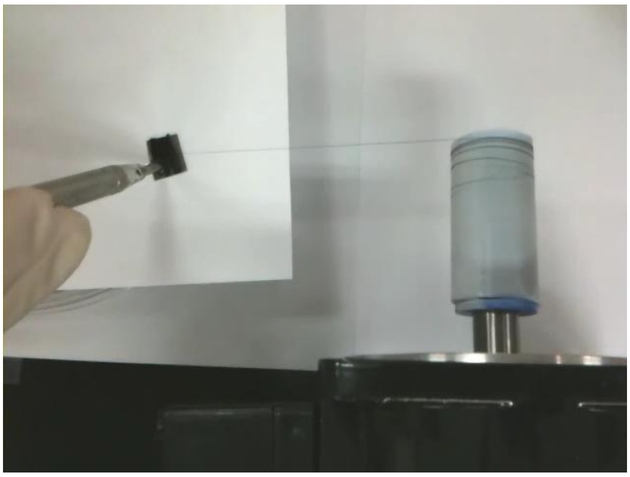
Fig. 2. CNT yarn being directly spun from a CNT forest.

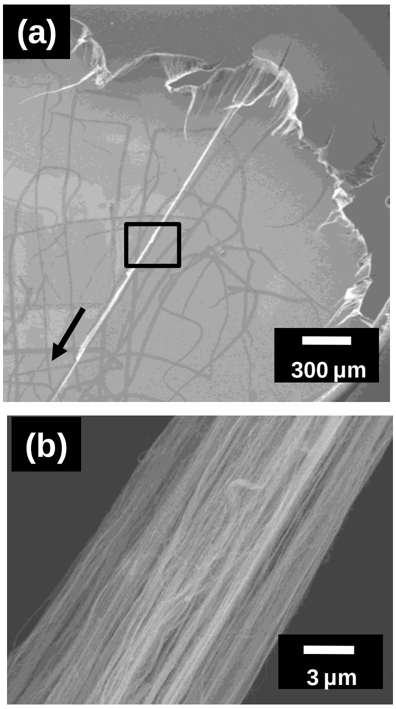

Fig. 3. SEM images of spinning CNT yarn from CNT forests (a) and enlarged image of the rectangular part (b)

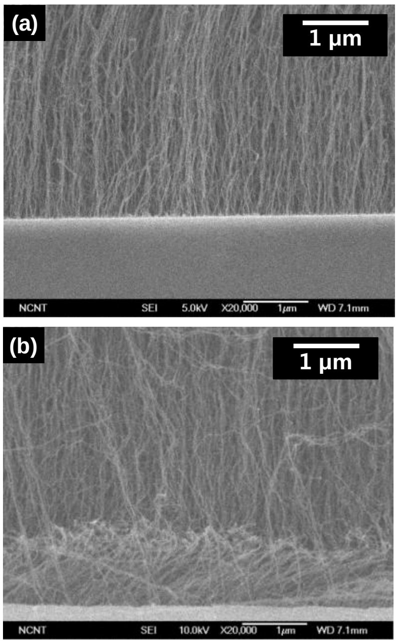

Fig. 4. SEM images of root region of CNT forests from thermal CVD process with (a) 'blowing-off' and (b) 'normal' termination process. Different morphology is observed at root region.

References

[1] V. Shanov and M. Schulz, Advancements in spinnable CNT arrays. Small Times 2009; 9(2): 24-27.

[2] M. Zhang, K. R. Atkinson, R. H. Baughman, Multifunctional carbon nanotube yarns by downsizing an ancient technology. Science 2004; 306: 1358-1361.

[3] K. Jiang, Q. Li, S. Fan. Spinning continuous carbon nanotube yarns. Nature 2002; 419: 801.

[4] X, Zhang, Q. Li, Y. Tu, Y. Li, J. Y.Coulter, Y. Zhu, et al. Strong carbon-nanotube fibers spun from long carbon-nanotube arrays. Small 2007; 3(2): 244-248.

[5] Q. Zhang, D. G. Wang, J. Q. Huang, W. P. Zhou, G. H. Luo, F. Wei, et al. Dry spinning yarns from vertically aligned carbon nanotube arrays produced by an improved floating catalyst chemical vapor deposition method. Carbon 2010; 48: 2855-2861.

[6] X. Zhang, K. Jiang, C. Feng, P. Liu, L. Zhang, S. Fan, et al. Spinning and processing continuous yarns from 4-inch wafer scale super-aligned carbon nanotube arrays. Adv Mater 2006; 18: 1505-1510.

[7] C.P. Huynh, S. C. Hawkins. Understanding the synthesis of directly spinnable carbon nanotube forests. Carbon 2010; 48: 1105-1115.

[8] Q. Li, X. Zhang, R.F. DePaula, L. Zheng, Y. Zhao, Y. T. Zhu, et al. Sustained growth of ultralong carbon nanotube arrays for fiber spinning. Adv Mater 2006; 18: 3160-3163.

[9] M. Zhang, S. Fang, A. A. Zakhidov, S. B. Lee, A. E. Aliev, R. H. Baughman, et al. Strong, Transparent, Multifunctional, Carbon Nanotube Sheets. Science 2005; 309: 1215-1219.