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Mist CVD process including successive deposition of Al_2O_3, Fe catalyst layers and carbon nanotubes for high density forest

T. Kinoshita[1], M. Karita[2], T. Nakano[2], Y. Inoue[2], T. Miwa[3] and H. Nagaoka[3]

[1] Graduate school of Science and Technology, Shizuoka Univ.
3-5-1 Johoku, Naka-ku, Hamamatsu, 432-8561, Japan
Phone: +81-53-478-1107 E-mail: kinoshita@cnt.eng.shizuoka.ac.jp
[2] Department of Electronics and Material Science, Shizuoka Univ.
3-5-1 Johoku, Naka-ku, Hamamatsu, 432-8561, Japan
[3] JNC Petrochemical Corp.
5-1 Goikaigan, Ichihara, 290-8551, Japan

Abstract

We have developed one-furnace chemical vapor deposition method for carbon nanotube (CNT) growth. Al_2O_3 catalyst support layer and Fe nanoparticle were deposited first by mist chemical vapor deposition (CVD), then CNT was grown by thermal CVD. We found that the Al_2O_3 supporting layer enhanced lifetime of catalyst activity resulting in 5 times longer CNT forest.

1. Introduction

Carbon nanotubes (CNT), having a nano-sized tubular structure, have been attracting much interests because of its good material properties. To utilize the good properties in industrial applications, it is required to have CNTs aligned in a direction. As a good way to align CNTs, the dry-spinning phenomena from a CNT forest has been investigated. CNT webs, in which CNT bundles are connected and aligned in the drawn direction, are formed by just drawing out a piece of the CNT forest, and it is easily composed into large scale CNT assemblies including CNT spun-yarn [1], CNT sheet [2] and CNT/polymer composite [3]. To grow such a spinnable CNT forest, high-density Fe catalyst nanoparticles are required to be formed on a substrate, and it is achieved by carefully controlled sputtering deposition of very thin Fe film. Therefore, the growth method of the spinnable forest is complicated.

On the other hand, a floating catalyst chemical vapor deposition (CVD) method has been developed for the CNT growth as simplified CVD method [4]. In this method, catalyst particles formation and CNT growth are conducted by simultaneously flowing a mixture of metal organic precursor and organic solvent. It doesn't require the pre-deposition of catalyst particles. However, certain amount of metallic impurity particles remains in CNT products [5]. Those CNTs need to be purified by acid treatments and it again makes CNT production process complicated.

In this study, we developed a modified floating catalyst CVD method in which process of catalyst formation and CNT growth were separated. First, Fe catalyst particles were formed by flowing mist of ferrocene, then CNT growth was followed by flowing acetylene. The method enabled to grow a high purity CNT forest with high spinning performance. In addition, we investigated effects of Al_2O_3 support layer for higher density of nanoparticles on a substrate. The Al_2O_3 layer was deposited by inserting deposition process before catalyst formation process. We found that the supporting layer enhanced the catalyst lifetime resulting in longer CNT.

2. Experimental

CNT forests were grown on oxidized Si wafers by modified mist-catalyst CVD (Fig. 1). In the growth procedure, Al_2O_3 support layer was first formed by flowing Al(III) acetylacetonate ($Al(acac)_3$) /ethanol mist [6]. The $Al(acac)_3$ solution (0.02 mol/L) mist was atomized by a ultrasonic nebulizer and supplied with a carrier gas of Ar onto the substrate in lateral quartz furnace heated at 500 °C. The mist CVD method is useful to supply low-vapor pressure species. Then, to form Fe catalyst nanoparticles on a substrate, the mist was switched to ferrocene/ethanol (0.5 mol/L) solution. The ferrocene mist was flown for 1.5 min at 700 °C. After these depositions, the furnace was purged and then acetylene was flown to grow CNT. CNTs were grown at 700 °C at 18 Torr until self-growth termination.

Chemical states of the Al deposition layer were analyzed by X-ray photo spectroscopy (XPS). Surface roughness of the Al layer was observed by atomic force microscopy (AFM). Morphology and purity of grown CNTs were examined by scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA).

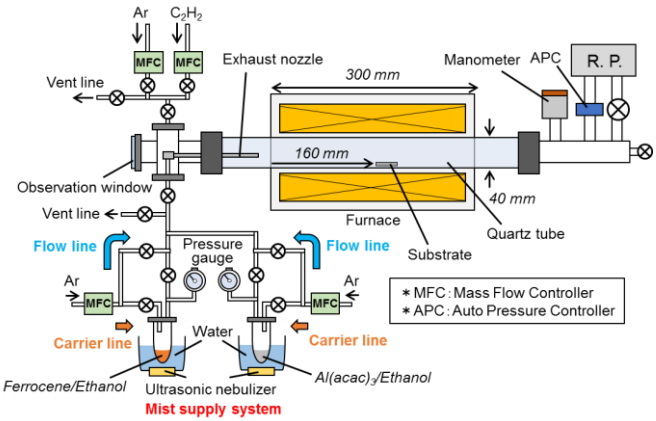

Fig. 1 Schematic illustration of mist CVD system. Al layer and Fe catalyst nanoparticles were deposited for CNT synthesis.

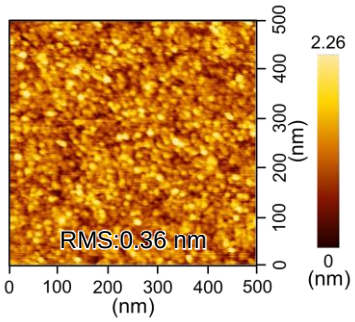

Fig. 2 AFM image of Al deposition layer.

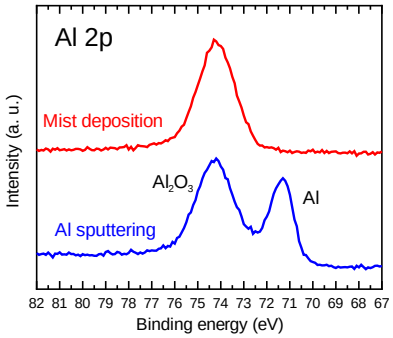

Fig. 3 Al 2p spectra of Al mist deposition layer and Al sputtering layer by XPS.

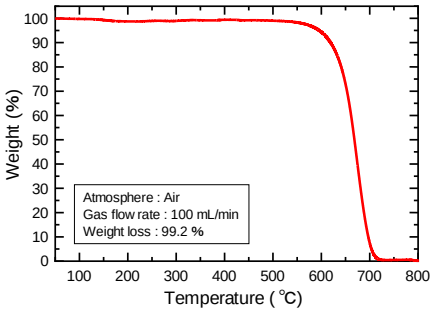

Fig. 4 TGA profile of grown CNT.

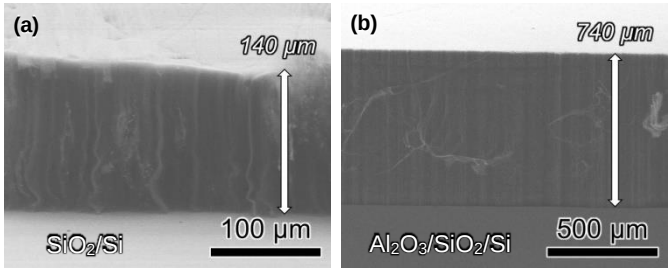

Fig. 5 Cross sectional SEM images of grown CNT forests on (a)SiO_2/Si substrate (no mist deposition of Al_2O_3 layer) and (b)Al_2O_3/SiO_2/Si substrate.

3. Results and discussion

Figure 2 shows an AFM image of an Al deposition layer. The surface is fully covered by nanoparticles. Surface roughness is as small as 0.36 nm. Deposition of nanoparticles was also confirmed by cross sectional SEM observation. It was found that 4 nm-thick layer was deposited on a SiO_2 layer. To investigate chemical states of the Al layer, XPS measurements were carried on the Al layer and on an Al sputtering layer for comparison purpose. Fig. 3 compares Al 2p spectra of mist CVD and sputtering films. For both spectra, Al oxide peak was observed, however metallic peak was only observed in sputtering film. This is indicative of that Al layer deposited by mist CVD was oxidized during the CVD process by reaction with ethanol.

Purity of a CNT forest was analyzed by TGA measurement as shown in Fig. 4. Estimated weight loss of a CNT sample was 99.2 %. Scanning transmission electron microscopy image of the CNTs shows no Fe particles in the CNTs. From these data, we found that the present modified mist CVD method gave pure CNTs forests with low Fe inclusion.

Figure 5 shows SEM images of CNT forests grown on SiO_2 layer and the Al_2O_3 layer. To see the maximum height of the forests, growth process was carried until self-growth termination. When CNT was grown on SiO_2 layer, forest height was 140 μm. On the other hand, the CNT forest on Al_2O_3 has 5 times longer height of 740 μm. These results clearly indicate that catalyst life time of Fe nanoparticles was significantly enhanced by inserting Al_2O_3 layer. However, CNT mean dimeter increased from 6.9 nm to 11.7 nm by depositing Al_2O_3 layer. CNT areal density was also decreased from 8.2×10^{10} cm^{-2} to 2.3×10^{10} cm^{-2}. To obtain highly spinnable CNT forests, it is very important to grow closely populated CNTs for strong bundling.

4. Conclusions

We established a modified mist CVD method for in-situ CNT synthesis. In this process, formation of Al_2O_3 layer and catalyst nanoparticle, and deposition of CNTs were successively conducted in one CVD chamber with no air exposure. It is possible to synthesize a high purity multi-walled CNT forest with high spinning performance. The present one-furnace synthesis process can be applied to roll-to-roll process as a continuous-growth technology of CNT on a flexible substrate, which is attractive as future industrial production. This study will contribute to CNT-based applications with large-scale CNT assemblies.

Acknowledgements

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