

Growth and characteristics of vertically-aligned carbon nanotubes by thermal CVD on various Si-based substrates for micro-DMFC

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Abstract

The synthesis of vertically-aligned carbon nanotubes (VACNTs) on various substrates with different catalyst/adhesion layers by thermal CVD is investigated in this research. The CNTs are employed not only as the catalyst carrier of micro DMFC to increase the surface area for reaction but also carry out nano-surface for rapid gas bubble removal to enhance reaction efficiency. As a result, not only the density and length of CNTs are important, morphology, such as alignment in specific direction, is also critical for performance enhancement. In this research, the properties of the CNTs on various catalyst/adhesion layers and the growth conditions by thermal CVD have been characterized on the size, morphology, density, wettability of the catalyst, and adhesion ability. The silicon-based substrate is able to be integrated into μ DMFC.

Keywords: Carbon nanotubes, Thermal CVD, Catalyst carrier, Micro DMFC, MEMS

1 - INTRODUCTION

Many researches for large-area well-aligned carbon nanotubes have been carried out, including multi-walled CNTs with controllable diameters and lengths on glass substrate [1], growth direction controllable CNTs on silica or silicon surfaces [2], single-walled CNTs synthesized on ultrathin Ni/Al bilayer film [3], and density controllable multi-walled CNTs on the metal catalyst/diffusion barrier layers [4, 5]. However, to increase the effective reaction area, reduce the catalyst loading, improve de-gassing property, and obtain reasonable adhesion between the substrates and CNTs are crucial in micro DMFC operation, but not mentioned in the previous works in a combination. In this paper, we investigate the catalyst/adhesion layers and process parameters for CNTs growth by thermal CVD to achieve high density and vertically aligned CNTs with decent adhesion and de-gassing properties for the application of μ DMFC.

2 - EXPERIMENTAL

2.1 - Catalyst fabrication

Si (100) substrates were grown with 100 nm thick thermal oxide or deposited with 150 nm thick CVD nitride layer as a buffer layer, and evaporated with Al, Ti or Al/Ti and Ni by e-gun evaporator as an electron conduction/adhesion layer and catalyst layer for CNTs growth, respectively. The catalyst thin film is then patterned by lithography for the designated growth area of the CNTs.

2.2 - Thermal CVD for CNTs

The CNTs were synthesized in a thermal CVD quartz tube by introducing a mixture of ammonia (NH_3) and carbon source gas ethylene (C_2H_4) at about 800 °C for 5-20 minutes at atmospheric pressure [6]. In our experiments, the morphologies of the CNTs were controlled by the fabrication parameters, such as the thickness of catalytic metal/adhesion layer film, the selection of different adhesion layers, the growth time, the growth process, and the substrate materials.

One typical fabricated patterned CNTs array is shown in Fig. 1, illustrating a vertically-aligned configuration with hollow tube structure. The inner, outer diameter, wall thickness, and Ni catalyst (The Ni signals were characterized from EDS) diameter are 6, 28, 11, and 35 nm, respectively.

2.3 - SEM/TEM measurement and adhesion test

The morphology and detailed structure of the CNTs were investigated by SEM (JEOL JSM-6330F, and JSM-6380), and TEM (JEOL JEM-2000 FXII/JEM-2010, LaB_6). The adhesion ability between the CNTs and the substrates was tested by the ultrasonic vibration.

3 - RESULTS AND DISCUSSION

The characteristics of CNTs growth on different catalyst/adhesion layers are depicted in detail in the following sections.

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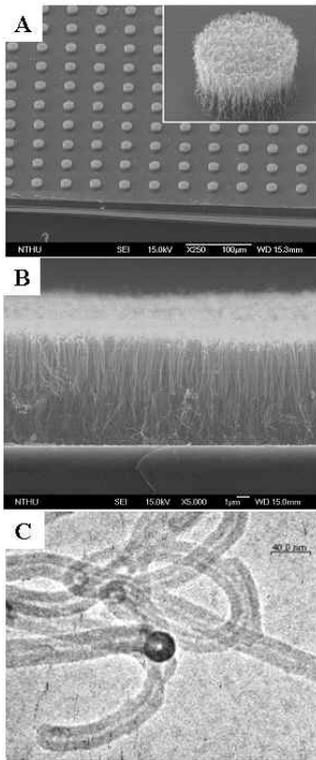


Figure 1 – (A) The patterned CNTs array illustrates 15 μm in diameter, 8.7 μm in height, 30 μm in spacing distance of each dot, (B) and (C) are the SEM micrograph and TEM image of the CNTs/Ni/bare Si substrate.

3.1 - CNTs growth on catalyst without adhesion layer

Catalytic nanoparticles - The Ni film deposited on the Si-based substrates was thermal-treated through the annealing process at 800 $^{\circ}\text{C}$ in a quartz-tube furnace. In Fig. 2, the morphology and density distribution of the annealed Ni nanoparticles (case 1) and their corresponding grown CNTs (case 2) on the Si-based substrates (A: bare Si, B: oxide, C: nitride surface) are illustrated, with a similar Ni particle size, larger contact angle ($B1 > A1 > C1$), better uniformity of the nanoparticle size ($B1 \approx C1 > A1$), and higher site density ($B1 > C1 \approx A1$) on the silicon oxide surface.

CNTs - Prior to the growth of the CNTs for 10 minutes, the better-aligned CNTs with higher density were both successfully synthesized on the bare silicon and oxide surfaces (A2, B2) compared to those on the silicon nitride surface (C2). A smaller diameter of the CNTs ($B2 < A2$) on the oxide surface may be attributed to a larger contact angle (B1), and the growth rate of the CNTs is faster ($B2 > A2$), as well as the aspect ratio (length and diameter ratio, L/D ratio) of the CNTs is also higher ($B2 > A2$), even grew longer for 20 minutes.

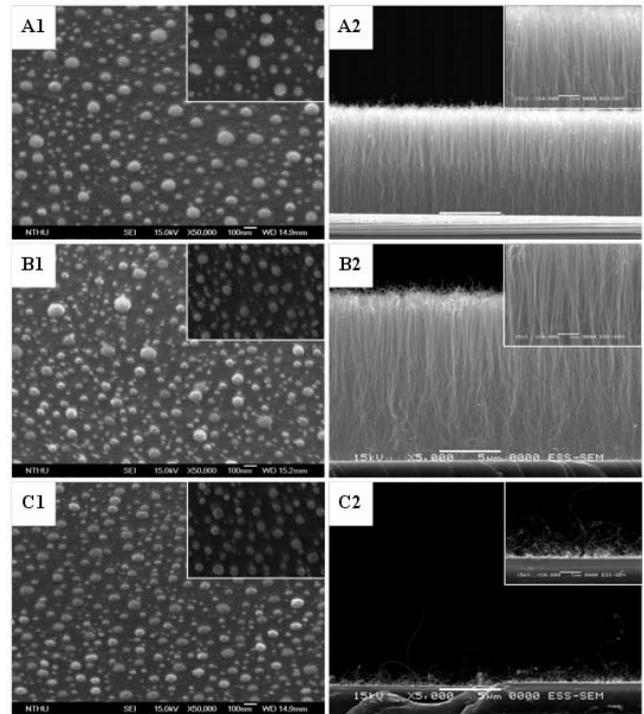


Figure 2 – The contact angle of Ni nanoscale catalysts (case 1) and the grown CNTs (case 2) on the Si-based substrates (A: bare silicon, B: silicon dioxide, C: silicon nitride). Insets are the higher SEM magnification.

3.2 - CNTs growth on catalyst with adhesion layer

For different thickness of Ni film on various adhesion layers, Figure 3 depicted the relationship between the growth rate and L/D ratio versus the growth time of the CNTs, suggesting a higher growth rate and L/D ratio of the CNTs on the basis of the thicker Ni catalytic layer without adhesion layer (A and B); A lower growth rate and L/D ratio of CNTs on adhesion layers, especially on the substrates with Al/Ti multilayers (D).

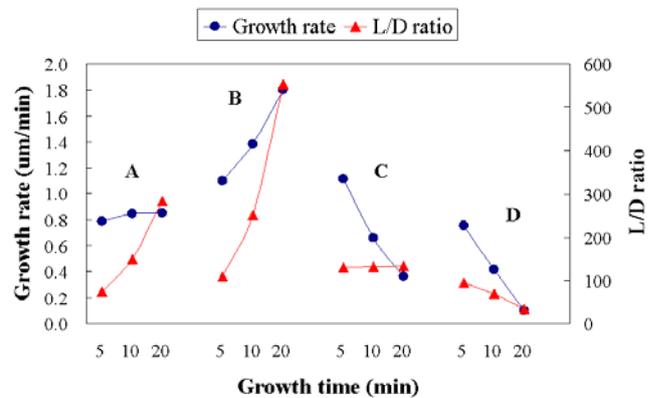


Figure 3 – Growth rate and L/D ratio of CNTs vs. growth time with/without various catalyst/adhesion layers (A) Ni: 5

nm/bare Si, (B) Ni: 10 nm/bare Si, (C) Ni: 5 nm/Al: 10 nm/bare Si, and (D) Ni: 5 nm/Al: 10 nm/Ti: 100 nm/bare Si.

Figure 4 showed the SEM images of the CNTs grown on different catalyst/adhesion layers. Without adhesion layer, taller CNTs can be obtained with thicker Ni catalytic layer (specimen B: 10 nm), which is twice as long as that on specimen A (5 nm thickness of Ni). Compare the specimens with adhesion layers with one another, the CNTs alignment and L/D ratio on Al are better than on Al/Ti multilayers, and even much better than on the surface of Ti only through the identical growth process.

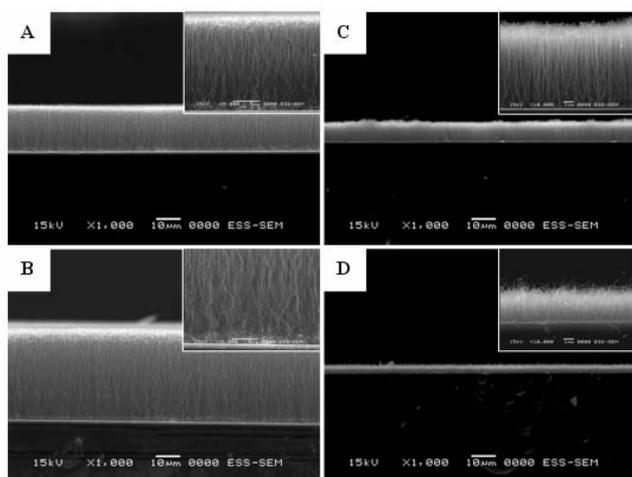


Figure 4 – The SEM images of CNTs grown on various adhesion layers for different growth time (A) Ni: 5 nm/bare Si (20 min), (B) Ni: 10 nm/bare Si (20 min), (C) Ni: 5 nm/Al: 10 nm/bare Si (10 min), and (D) Ni: 5 nm/Al: 10 nm/Ti: 100 nm/bare Si (5 min). Insets are the higher magnification of SEM images.

3.3 - Improvements of the growth of vertically-aligned CNTs

According to the aforementioned results, in order to improve the alignment and L/D ratio of the CNTs to acquire much larger reaction surface area, a modified two-step CNTs growth process, including gas flow and stationary conditions were adopted respectively, instead of continuous carbon gas flow. Figure 5 (A)-(C) demonstrated that the employment of Al as the adhesion layer providing a well-vertically aligned CNTs on the silicon nitride substrates with/without Ti layer through the two-step growth approach for totally 20 minutes growth time. And the length of CNTs with Al supported is also twice times longer than that with Ti only. In addition, compared to CNTs growth on bare silicon, the growth rate and L/D ratio of CNTs with Al, Ti or Al/Ti on the nitride surface are also much higher.

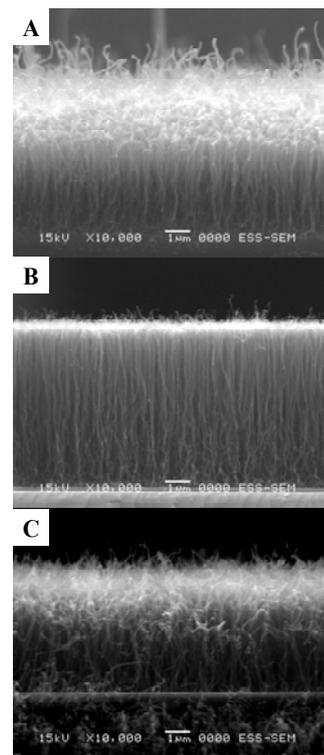


Figure 5 – SEM micrographs of the CNTs growth on various multilayers based on silicon nitride substrates (A) Ni: 5 nm/Al: 10 nm/Ti: 75 nm, (B) Ni: 5 nm/Al: 10 nm, (C) Ni: 5 nm/Ti: 100 nm.

3.4 - Growth mode of the VACNTs

The structure details of the CNTs were investigated using TEM and EDS. From the low magnification TEM images shown in Fig. 6 (A)-(D), it is visible that most of the Ni nanoparticles (EDS revealed that these nanoparticles mainly contained Ni, which can provide nucleation sites for the CNTs growth) were at the top tips of the VACNTs grown on the Al/silicon nitride substrate (the corresponding SEM micrographs refer to Fig. 5 (B)). The higher magnification TEM images in Fig. 6 (E), and (F) show that the catalytically-grown CNTs are multiwalled and bamboo-like structures, and the CNTs diameter and density distribution on the top are thicker and higher than those on the middle and base parts, respectively. It is suggested that the CNTs growth mechanism belongs to the tip-growth mode in this case.

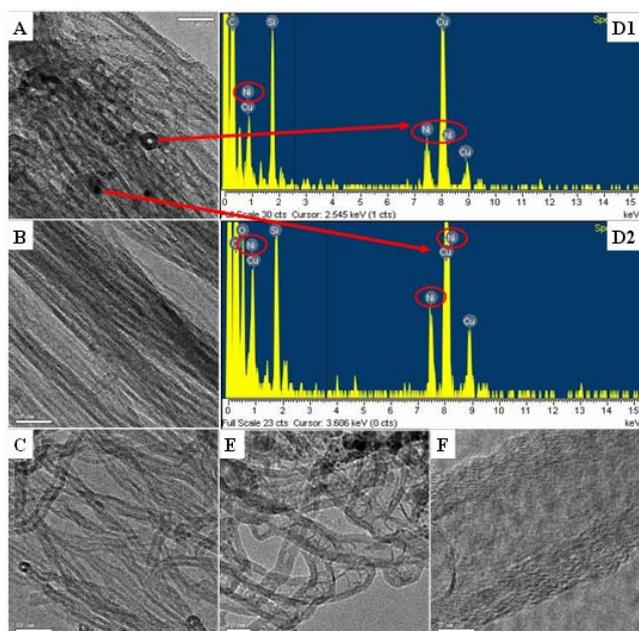


Figure 6 – TEM images and EDS of the VACNTs growth on Al layer based on silicon nitride substrates.

3.5 - Adhesion property measurements

Ultrasonic vibration test was performed on the working pieces with-/without adhesion layer for 1.5 minutes, and the SEM photos show that CNTs are peeled off easily for the one without adhesion layer while remaining very well on adhesion layers (Al/Ti or Ti only shown in Fig. 7). Otherwise, the CNTs with Al after the adhesion test, some of which were still keep the original configuration on the substrate, but others were peeled off.

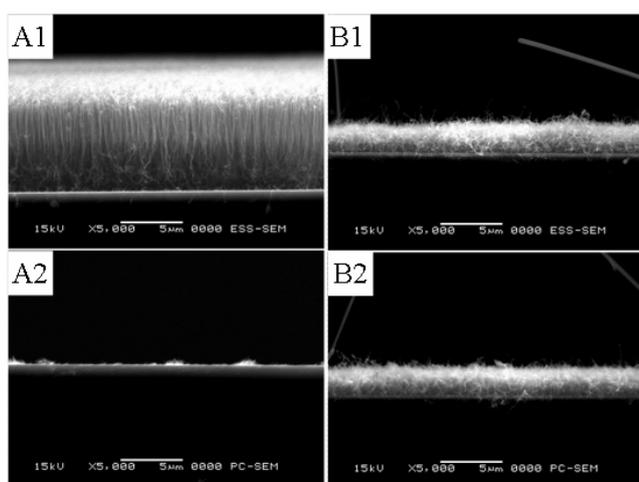


Figure 7 – SEM images (A) without, (B) with Ti layer on the substrates (1) before and (2) after the ultrasonic vibration test.

4 - CONCLUSIONS

In micro DMFC, high-aspect-ratio CNTs with specific growth direction play a crucial role as the electrocatalysis carrier, not only for the dramatical enhancement of the reaction area, but also the improvement of outgas capability. This paper demonstrated that by employing aluminum as the adhesion layer for nickel catalyst, not only the adhesion between the CNTs and the substrates can be much more improved, but also the straightness as well as L/D aspect ratio of CNTs were greatly improved by a two-step thermal CVD process. This enhancement may attribute to the smaller droplets formation of aluminum melted at low temperature during the CNTs growth process, which provides the citations for the formation of smaller/denser nickel nanoparticles resulting in the growth of aligned/straight CNTs. On the other hand, the second gas stationary step in the growth process to allow diffusion dominating in the perpendicular direction to the substrate also help on the growth of straight CNTs. The well-aligned/adhered CNTs and silicon-based materials can be easily integrated with MEMS structures for μ DMFC.

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