Stacked Self-standing Carbon Nanotube Forest Films Utilizing Periodical Multi-layered $(Fe/AlN)_n$ Films

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ABSTRACT

A novel carbon nanotube structure, stacked self-standing carbon nanotube forest films, were achieved by the catalytic thermal CVD for the periodically deposited multi-layered $(Fe/AlN)_n$ films. It was found that the high density, vertically oriented CNTs were grown on both side of the thin AlN film layers based on the bottom growth mode, and each AlN layers were separated by the high-density CNT growth, resulting in the formation of the stacked self-standing CNT forest films supported by the thin AlN films.

Keywords: carbon nanotube, carbon nanotube forest films, self-standing carbon nanotube forest films, periodical multi-layered catalyst films

1 INTRODUCTION

Carbon nanotubes (CNTs) [1] have attracted much attention of researchers because of their excellent electrical, physical and chemical properties. CNTs forest films uniform in length are expected for bulk applications such as the high-surface-area electrode for the electric double layer capacitor (EDLC)[2], Micro Electro Mechanical Systems (MEMS) [3], field emitter for lamps[4, 5], bio-substrate etc. Self-standing stacked CNT films have also attracted as new structures for the new applications of the electronic, mechanical, and chemical and bio devices. Multi-stacked CNT forest films were reported by Zhu[6], which was achieved by the technique of periodical growth and cut of CNTs by the oxidization of the CNT-catalyst interfaces. Li reported[7] multi-stacked CNT forest films achieved by the periodical growth of CNTs and Fe catalyst deposition on the top surface of the CNT forest using the ferrocene gas. In this report, we will discuss the formation mechanism on a novel CNT structure, stacked self-standing CNT forest films achieved by CNT growth on periodically deposited multi-layered (Fe/AlN)n catalyst films.

2 EXPERIMENTAL

Fe and AlN films were deposited periodically on the thermally oxidized Si substrates by magnetron sputtering method without breaking vacuum to prepare $(Fe/AlN)_n$ multi-layered films as shown in Fig. 1. Sputtering conditions including the thickness of Fe and AlN film layers are summarized in Table 1.

Catalytic thermal CVD were carried out for the growth of CNTs on the $(Fe/AlN)_n$ multi-layered catalyst films at the growth temperature of 730 °C using acetylene (C_2H_2) as a carbon feed gas.

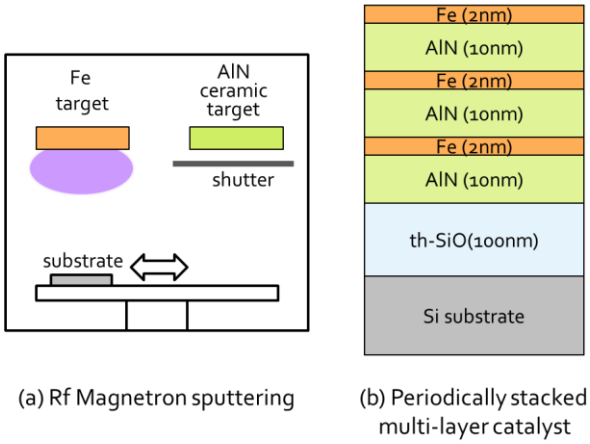

Figure 1: (a) Schematic of the magnetron sputtering system for the deposition of (b) the periodically stacked multi-layered $(Fe/AlN)_n$ catalyst films.

	Conditions
Method	RF magnetron sputtering
Substrate	Thermally oxidized Si (100nmSiO_2 on Si)
Target	Fe (2mm thick) > 99.99 %, AlN Ceramic (5 mm thick) > 99.9 %
Target size	3 inch ϕ
Sputtering gas	Ar 30 sccm
Gas pressure	3 Pa
RF power	200W for Fe, 100W for AlN
Film thickess	0.5, 1.0, 2.0 nm for Fe, 0.75, 1.5, 3, 10 nm for AlN

Table 1: Sputtering conditions for the periodiccaly stacked multi-layered catalyst films on th-SiO/Si substrate.

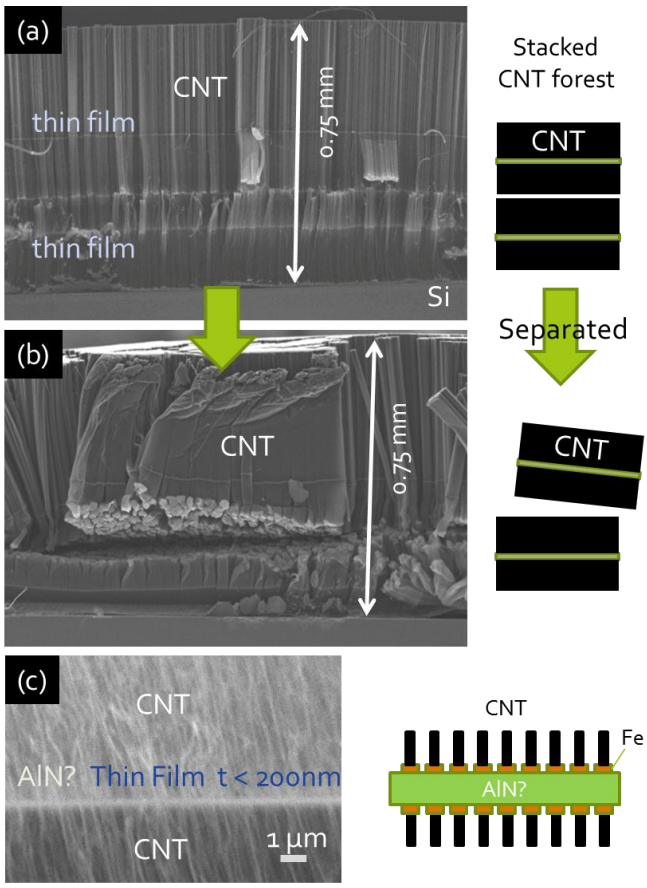

Figure 2: (a) Cross-sectional SEM image of the CNT forest grown by the (Fe/AlN)n catalyst on the th-SiO_2 substrate and (b) separated CNT forest films. (c) The high-magnified view and schematic of the multi-stacked CNT forest films in the area at the thin film in (a).

3 RESULTS AND DISCUSSION

Figure 2 (a) shows the SEM image of the cross sections of the CNT forest grown on the $(Fe/AlN)_n$ catalyst films. The thickness of the Fe and AlN layers were 2 and 10 nm, respectively. The CNT forest looked constructed with the multi-stacked vertically aligned CNT forest films. The each stack of CNT films could be easily separated by hand as shown in Fig. 2(b). Figure 2(c) shows the high-magnified cross-sectional view of a CNT forest layer in the stacked forest films. At the center of the CNT forest layer, a thin film was observed as shown in Fig. 2(c). It could be noticed that the carbon nanotubes were grown on both sides of the thin films in the base growth mode. A schematic model of the CNT growth on both sides of the thin film was shown in Fig. 2(c).

The elemental composition mappings of the multi-stacked CNT forest films were carried out with SEM-EDX (HITACHI) to clarify the location of the Fe catalysts and the composition of the thin films located at the middle of the CNT forest layers. Figure 3 shows the SEM image and corresponding EDX mapping images for Al and Fe elements. Two kinds of layers, consisted with only Al, or both of Fe and Al, were observed as shown in Fig. 3(b, c). Comparing of the Al and Fe elements maps revealed that Al elements were concentrated at the thin films layers, and Fe elements were located both at the thin films and at the edge face of each stacked CNT forest films.

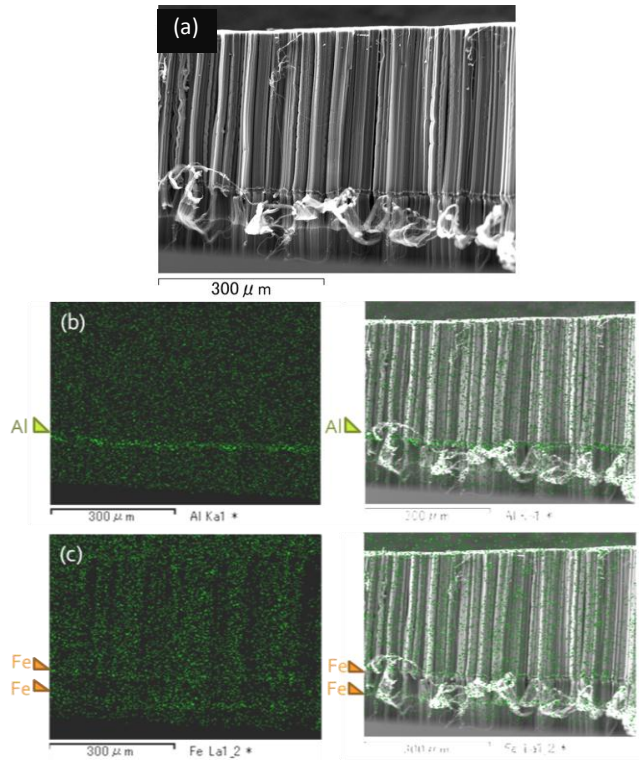

Figure 3: (a) Cross-sectional SEM image of the stacked CNT forest films. The EDX mapping images and their superimposed images on SEM images are shown for (b) Al and (c) Fe elements, respectively.

It should be emphasized that the top surface of the $(Fe/AlN)_n$ multi-layered catalyst must be consisted of Fe; otherwise, any CNTs could not be grown on the $AlN/(Fe/AlN)_n$ catalyst surface. Figure 4 shows the SEM images of the top surface of the $AlN/(Fe/AlN)_5$ catalyst films after the CVD process with the CNT growth condition. The CNT growth was not observed at the surface of the $AlN/(Fe/AlN)_5$ films excluding at the scratches on the surface.

The growth condition of the multi-stacked CNT forest films, dependent on the thickness of the AlN supporting film layers, were investigated using the $(Fe/AlN)_{10}$ catalyst films with the varying AlN film thickness from 0.75 to 3.0 nm, and the varying Fe film thickness from 0.5 to 2 nm. The growth lengths on each film are summarized in Table 2.

The CNT growth length of the forests increased with decreasing the AlN layer thickness. On the other hand, the CNT length increased with increasing the Fe layer thickness. We interpreted as follows. The volume density of the Fe nano-particles on the each AlN layers increased with decreasing the AlN layer thickness, resulting in the longer CNT growth in 1.5 mm length for the (Fe(1nm) / AlN(0.75nm)) $_{10}$ catalyst.

Figure 6 shows a growth model based on the observation by SEM-EDX. Carbon atoms, which were decomposed from acetylene gas at the top surface of the $(Fe/AlN)_n$ catalyst (Fig. 6(a)), diffused into the closest Fe layers through the AlN thin films (Fig. 6(b)). The carbon atoms penetrated to the deeper inner Fe layers and formed CNTs on the Fe catalyst particles in base-growth mechanisms (Fig. 6(c)). Finally, each AlN layers was separated by high density, vertically aligned CNTs, resulting in the formation of the stacked self-standing CNT forest films (Fig. 6(d)).

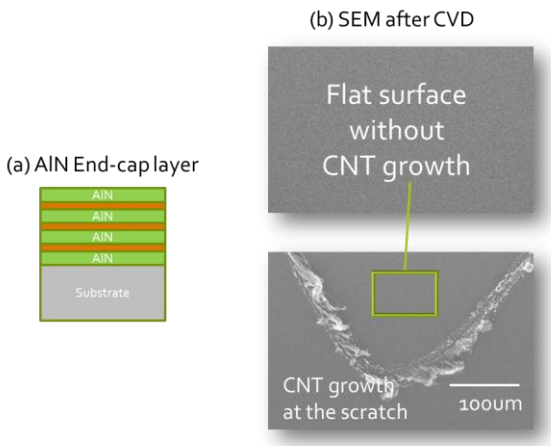

Figure 4: (a) A schematic of the AlN end-capped AlN/(Fe/AlN)n multi-layered films. (b) SEM images of the top surface of the $AlN/(Fe/AlN)_5$ catalyst films after the CVD. CNT growth was not observed at the top surface of $AlN/(Fe/AlN)_5$ films excluding at the scratches on the surface.

Fe / AlN thicknesses	CNT growth length in the CNT forest films
2.0 / 10 nm	0.2 mm *
1.0 / 3.0 nm	0.2 mm
1.0 / 1.5 nm	0.2 mm
1.0 / 0.75 nm	1.5 mm

* shown in Fig. 2(a)

Table 2: CNT length grown on the $(Fe/AlN)_n$ films with the varied AlN thickness of 3.0, 1.5, and 0.75 nm. CNT length shown in Fig. 2(a) is also listed.

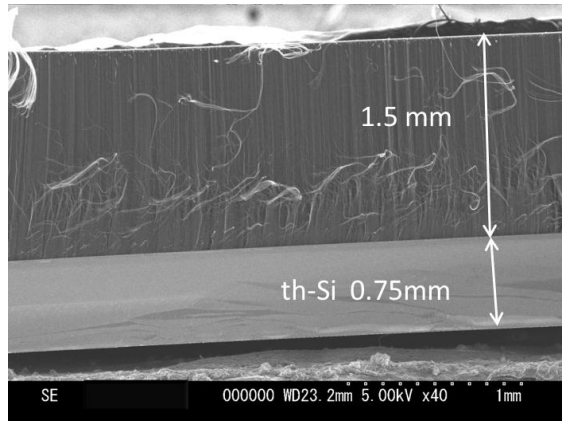

Figure 5: Cross-sectional SEM image of the CNT forest grown on the $(Fe(1\ nm)/AlN(0.75\ nm))_{10}$ films. The base part of the CNT forest was connected to the substrate and stacked CNT forest film structures were not observed.

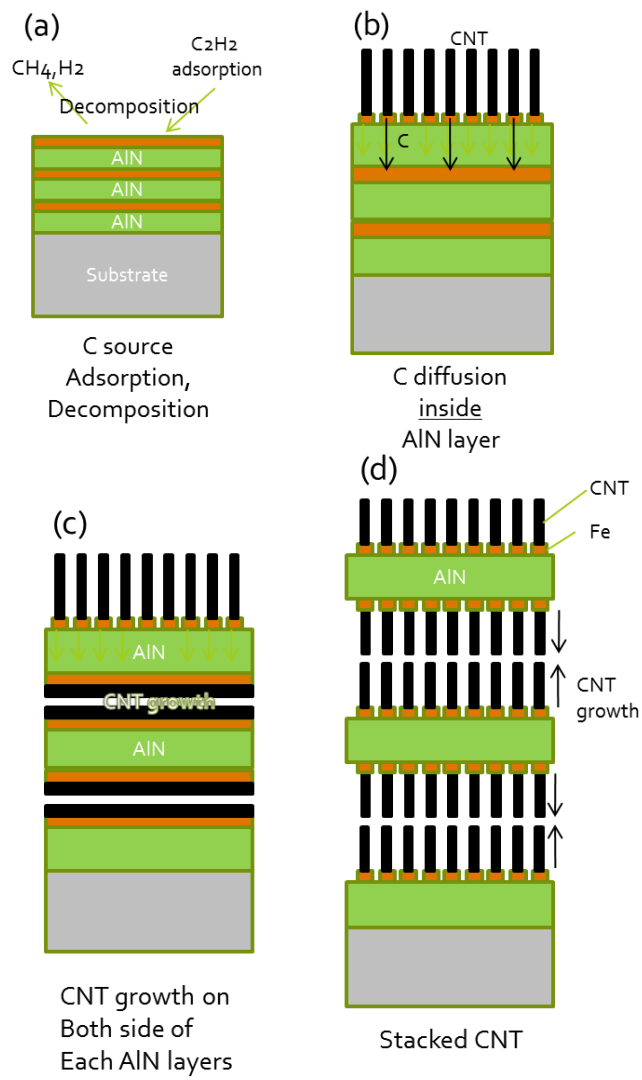

Figure6: Growth model of the Stacked CNT forest films.

4 CONCLUSION

A novel CNT structure, self-standing vertically alighned CNT films were obtained by using periodically multi-layered (Fe/AlN)x catalyst films. The stacked self-standing CNT forest films is expected to be applied in the applications of thermal conducting sheet, electrical contact sheet, base substrate for bio applications, etc.

5 ACKNOWLEDGEMENT

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