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Millimeter-tall carbon nanotube arrays grown on aluminum substrates

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ABSTRACT

Millimeter-tall vertically aligned carbon nanotubes (VA-CNTs) were grown directly on Al substrates. Atmospheric pressure chemical vapor deposition is performed at 600 °C, which is well below the melting point of Al (660 °C), using Fe catalyst and C_2H_2 as a highly reactive carbon feedstock. The CNT height was sensitive to the C_2H_2 concentration and 0.06 vol% was optimum for balanced growth rate and catalyst lifetime, yielding 0.06 mm-tall VA-CNTs in 2 h. The CO_2 addition at 1.8 vol% to the C_2H_2/Ar gas significantly enhanced the CNT growth, yielding 1.1 mm-tall VA-CNTs in 12 h. CO_2 shows this remarkable effect when added in large excess to C_2H_2, differently from the well-known method of "small addition of water." Moreover, the resulting VA-CNTs showed electrical contact with the Al sheets with resistance of $\leq 0.7\ \Omega\ cm^{-2}$. The effect of CO_2 is systematically studied and discussed.

1. Introduction

Carbon nanotubes (CNTs) have attracted great interest for various applications, e.g., heat transfer materials [1,2] and electrochemical energy storage devices [3,4], due to their high thermal and electrical conductivities. Metal foils and plates have been widely used in such applications, and many groups have studied direct growth of vertically aligned CNTs (VA-CNTs) on metal substrates by chemical vapor deposition (CVD) to realize better interfacial contacts with solid surfaces or to expand the surface from two to three dimensions. For example, VA-CNTs/Cu for thermal interface materials [5–8] and VA-CNTs/Al for electrodes of electric double-layer capacitors [9–16] have been reported. Although millimeter-tall VA-CNTs have been realized on Cu substrates [17] and on non-metallic substrates such as SiO_2/Si or SiO_2, the CNT height remains at ~100 μm or less on Al substrates.

VA-CNTs were reported first for multi-wall CNTs (MWCNTs) using Fe catalyst supported on mesoporous silica particles [18], quartz glass [19] or on porous-Si/Si substrates [20]. But several years were needed to realize such growth for single-wall CNTs (SWCNTs) [21,22]. The "water-assisted CVD" method enables the growth of millimeter-tall VA-CNTs in tens of minutes using H_2O vapor as an additive [22,23]. H_2O is thought to prolong the catalyst lifetime by etching carbon byproducts covering and deactivating catalyst particles and/or by suppressing Ostwald ripening of the catalyst particles [24]. The effectiveness of adding oxygen-containing species during the growth have been also confirmed with other cases such as C_2H_5OH [21,25,26], CO [27], CO_2 [28–30], and O_2 [31]. But such etching gas is not always needed if the carbon feed is moderated [32,33]. C_2H_2 is known as an effective direct growth precursor [34–36], and its partial pressure should be lowered for lower temperatures to prevent carbonization and deactivation of the catalyst particles [37,38].

Typical growth temperature in these methods is usually set to around 700–800 °C which enables the growth rate as high as 3–5 μm s^{-1} [39]. Si or quartz glass substrates combined with insulating layers (SiO_2 or Al_2O_3), which can tolerate high growth temperature, are widely used for the millimeter-tall VA-CNT growth. Among various metals, Al is important due to its high thermal and electrical conductivities, small mass density, chemically stable passivated surface and low cost. But it has a very low

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melting point of 660 °C and therefore millimeter-tall VA-CNTs on it is still challenging and have not been reported to date. Fig. 1a shows the relationship between the growth time and the maximum height of the VA-CNTs on Al substrates and foils reported in the previous works (black symbols) [9,12–16,40–44] and the present work (red and blue symbols). Detailed information (catalyst design, growth temperature, total gas pressure, carbon precursor, CVD time, and height of obtained CNTs) of the previous works are shown in Supplementary data Table S1. Despite years of studies, the growth rate is as small as a few μm min^{-1} or less, and the maximum height has been limited to 100 μm. All the catalytic processes including dissociative adsorption of the carbon sources on, diffusion of carbon species through/over, and precipitation of carbon to CNTs from the catalyst particles become exponentially slower for lower process temperatures, which makes it much more difficult to grow taller VA-CNTs on Al substrates and foils.

Here, we report the growth of millimeter-tall VA-CNTs on Al substrates (Fig. 1b). Due to the low melting point of Al, all the CVD runs were carried out at 600 °C under atmospheric pressure. We selected C_2H_2 as a carbon feedstock, which is highly reactive and works at temperatures as low as 400 °C [38], and Fe as a catalyst without any buffer layers except for a native oxide layer. The effect of Fe catalyst thickness on the CNT growth was systematically investigated by our combinatorial masked deposition (CMD) method [45]. We also supplied CO_2 during CVD, and found it effective to enhance the VA-CNT growth on Al substrates to reach 1.1 mm in 12 h. The VA-CNT growth on Al substrates is compared with that on SiO_2/Si substrates and the mechanisms for catalyst particle formation and CNT growth are discussed.

2. Experimental

2.1. Substrate and catalyst preparation

The method for the deposition of the catalyst films is described in our previous work [45]. Briefly, Al sheets with a thickness of 0.20 mm (99.9% purity, Nilaco, Tokyo, Japan) were cut to 15 mm × 5 mm and used as substrates without any surface treatment. Fe was deposited directly on the Al substrates by radio frequency magnetron sputtering with Ar (1.3 Pa). Fe thickness (t_{Fe}) had a uniform profile or a gradient profile ranging from 0.3 to 8 nm by using the CMD method [45]. As a reference, SiO_2 (90 nm)/Si substrates with the same size (15 mm × 5 mm) were also used without any surface treatment. On the SiO_2/Si substrates, Al (15 nm) was deposited by sputtering and exposed to air to form an aluminum oxide layer (AlO_x), and then Fe with the thickness gradient was deposited by the CMD method. The catalyst-deposited substrates were transferred to a CVD furnace by breaking the vacuum.

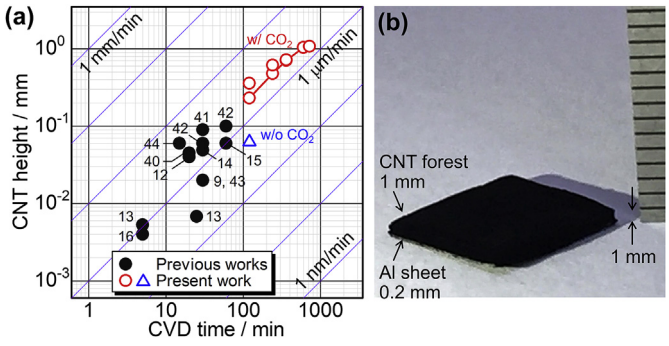

Fig. 1. (a) Comparison of the VA-CNTs on Al substrates of the present work (red open circle and blue triangular symbols) with those in the previous reports (black closed symbols) [9,12–16,40–44]. The data of the previous works are based on the information in Table S1 and each number in the graph shows the reference. Red open circle/blue triangular symbols correspond to the results of the CNT growth with/without supplying CO_2 in this work, respectively, and the tallest VA-CNTs (1.1 mm) grew in 12 h in this work. (b) 1 mm-tall VA-CNTs grown on a 0.2 mm-thick Al sheet in 10 h. (A colour version of this figure can be viewed online.)

2.2. CNT growth and characterization

The samples were loaded onto a quartz-glass plate in a quartz tubular reactor (inner diameter of 34 mm and heating zone length of 300 mm) with one end closed [46]. The samples were heated in 10 min from room temperature to 600 °C and held for 5 min at 600 °C under 10 vol% H_2 diluted by Ar with a total flow rate of 500 sccm to reduce Fe and form nanoparticles. For all experiments in this work, Ar was used as a carrier gas, and the total flow rate of the gas was set to 500 sccm during annealing and CVD processes. Then, the gas was switched to 0.03–0.1 vol% C_2H_2/10 vol% H_2/Ar to start the CNT growth. All the annealing and CVD processes were conducted at 600 °C under the ambient pressure with or without 0.6–6.0 vol% CO_2. We also monitored the CNT growth on real time through a glass window at the end of the reaction tube using a digital camera during the CNT growth [33,39], and analyzed the growth rates of VA-CNTs at different t_{Fe}. After the growth, the heater was turned off and the samples were cooled down to room temperature under Ar flow (~400 sccm). The height and the structures of the as-grown VA-CNTs were characterized by scanning electron microscope (SEM; Hitachi S-4800, Tokyo, Japan) and transmission electron microscope (TEM; JEOL JEM-2100F, Akishima, Japan). The quality of CNTs was characterized by Raman spectroscopy (Horiba HR-800, Kyoto, Japan) with an excitation wavelength of 488 nm.

2.3. Characterization of catalysts on substrates

To investigate the effect of CO_2 on the formation of Fe catalyst nanoparticles, we compared the Fe catalyst on Al and AlO_x/SiO_2/Si substrates after annealing with H_2 or H_2/CO_2. Chemical states of each component were analyzed ex situ by X-ray photoelectron spectroscopy (XPS; JEOL JPS 9010MX, Akishima, Japan), and the number densities and heights of catalyst particles were measured ex situ by atomic force microscope (AFM; Shimadzu, SPM 9600, Kyoto, Japan). After removing CNTs by scotch tape, the cross sections were prepared for the Fe/Al samples after CNT growth by depositing protective carbon layer on the sample surface followed by focused ion beam (FIB; JEOL JIB-4000) and analyzed by scanning transmission electron microscope (STEM; JEOL JEM-2100F) equipped with energy dispersive X-ray spectrometer (EDS; JEOL JED-2300T). The CNT/Al interface of the samples after CVD was exposed to the surface by lift-off method and analyzed by SEM (S-4800) equipped with EDS (Ametek EDAX Genesis, Elancourt, France).

3. Results and discussion

3.1. Optimization of C_2H_2 concentration for CNT growth on Al substrates and growth enhancement by CO_2

Firstly, C_2H_2 concentration was optimized to grow taller CNTs without adding CO_2. Fe catalysts with a gradient thickness profile were sputter-deposited on Al substrates by the CMD method [45] (Fig. 2a–c). The samples were set in a tubular CVD reactor, heated in 10 min to and held for 5 min at 600 °C under 10 vol% H_2/Ar at ambient pressure, and then C_2H_2 was added to start the CNT growth. CNTs grew vertically to tens of micrometers in height in 2 h