CARBON 87 (2015) 453–461

Available at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/carbon

Synthesis of vertically aligned single-walled carbon nanotubes with metallic chirality through facet control of catalysts

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ARTICLE INFO

Article history:
Received 31 October 2014
Accepted 13 February 2015
Available online 21 February 2015

ABSTRACT

For nanotube synthesis, iron platinum (FePt) alloy particles have been prepared on a single crystalline magnesium oxide (MgO) substrate by alternate sputter deposition of FePt and MgO. Partially facetted {111}-nano particles of FePt have been epitaxially formed on the substrate and periodically exposed on the surface. The particles of FePt were half-buried between deposited MgO showed superior thermal stability and microparticulations were also achieved by optimization of film layer thickness. By using the substrates for growth of carbon nanotubes, vertically aligned single-walled carbon nanotubes (forest) have been successfully grown on the substrate containing the faceted FePt nanoparticles. Raman spectra of the forest have revealed prominent features of metallic nanotubes in the radial breathing-mode region.

1. Introduction

Carbon nanotubes (CNTs) consist of carbon molecules that form a simple cylindrical structure having novel electrical and mechanical properties. They have been widely studied as a representative nano material for various future applications [1]. Among them, vertically aligned CNTs (the so-called "forest") have been extensively investigated because they offer advantages such as good alignment, ease of purification for catalyst removal (because catalysts usually remain on the substrate after removing the forest from the substrate), and easy handling of the synthesized CNTs for making composites as functional materials. Significant effort has been devoted to achieve forests not only of multi-walled carbon nanotubes (MWCNTs) [2–4] but also those of single-walled carbon nanotubes (SWCNTs) [5–7]. In keeping with these researches, using the basic concepts of a sandwich catalyst, Al_2O_3/Fe/Al_2O_3, and antenna-type remote plasma chemical vapor deposition (ARPCVD), we have identified the composition of the catalyst and optimization of process parameters to be indispensable factors for the synthesis of SWCNT forests [8,9]. Moreover, by adding titanium to the abovementioned sandwich catalyst, we have successfully synthesized unprecedented SWCNT forests composed of individual nanotubes having millimeter lengths and small diameters (about 1.3 nm) [10].

It is well-known that the structure of SWCNTs can be defined by chiral indices (n, m). The challenge about a separation technique for obtaining pure (n, m) SWCNTs after synthesis (a "post-synthesis method") was recently improved and some limited single-chirality SWNTs have been obtained [11–14]. Nevertheless, direct synthesis of specific SWCNTs

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http://dx.doi.org/10.1016/j.carbon.2015.02.051
0008-6223/

continues to be intensively explored because the post-synthesis method involves a complicated separation process and a separation medium (i.e., a surfactant is necessary for the separation, which becomes a contaminant). In fact, selective syntheses of SWCNTs using transition metal catalysts, such as Fe, Co, and Ni, have been frequently reported to yield near-armchair SWCNTs composed of semiconducting tubes such as chiral (6, 5), (7, 5), and (9, 8), mainly [15–22]. It has also been suggested that the structure of a catalyst, such as a facet, affects the chirality of SWCNTs [16]. Early, a computational study revealed that there is a structural relationship between a {1 1 1}-facet of Ni and metallic SWCNTs such as armchair (5, 5), zigzag (9, 0), and zigzag (12, 0) [23]. Actually, using TEM with atomic-level resolution, the analogy between {1 1 1}-facet of Co and structure of SWNT was suggested [24]. In addition, the selective synthesis of metallic SWCNTs involved the formation of a {1 1 1}-facet of Fe using a small amount of water vapor during the pretreatment of the catalyst just prior to synthesis [25].

However, the discussion about the structural relationship between a catalyst and a nanotube remains somewhat controversial since it is not easy to confirm the state of the catalyst (i.e., solid or liquid). Moreover, the metal has a lower melting point at nanoscale than in bulk. In particular, on the synthesis using CVD normally operated at high temperature over 1073 K, it is thought to be unavoidable to stop the change of catalyst morphology during the synthesis. From this perspective, recently, some studies have been reported on highly selective syntheses of near-armchair SWCNTs involving *solid* catalysts such as single crystalline BN (boron nitride) [26], $Co_xMg_{1-x}O$ solid solutions [27], $CoSO_4/SiO_2$ [28], and W_6Co_7 [29]. In these studies, the chirality of nanotubes is considered to be strongly affected by structures such as an atomic step and/or atomic ordering of those *solid* catalysts during the growth of the SWCNTs.

As mentioned above, extensive research continues on selective syntheses. In these researches, based on the both usage of thermally stable solid catalyst and synthesis of CNTs at low temperature, the possibility for structure–control of CNT by the direct synthesis is suggested. However, the methods reported so far yield only a part of the chirality region, the near-armchair region. Moreover, combining with the difficulty of arrangement of nano-particle catalyst with high-density on the substrate, the resulting SWCNTs are usually not aligned and have low density compared to that of a forest on the substrate. To realize a selective synthesis for metallic SWCNTs with unparalleled high density (as a forest), we have first tried the combination of the {1 1 1}-facet of a catalyst with thermal stability and ARPCVD that is possible to synthesize CNTs at low temperature under 1073 K.

As fabrication methods for Fe-based nanoparticles with faceting control, magnetic nanoparticles through polyol (wet process) have been widely investigated and several size- and facet-controlled particles have been successfully fabricated [30,31]. In addition, syntheses of CNTs using alloy particles consisting of transition and precious metals (e.g., FePt, FeRu) have been reported [32]. However, if surfactant-coated nanoparticles prepared using the polyol method are simply adopted for high-density assembly of nanoparticles on ordinary substrates (e.g., a silicon wafer), nanoparticle coarsening cannot be avoided during the synthesis of CNTs at high temperatures [33] by not-enough stabilization of thus prepared substrates; this may be considered to be a limitation of this wet-process approach. Therefore, we focus on facet control of the catalyst through sputtering deposition (dry process), which is commonly used in the studies of magnetic materials. In fact, it has been reported that faceted FePt particles can be fabricated in a floating gas by controlling parameters (e.g., input power, gas pressure) during sputtering [34]. Preparation of {1 1 1}-faceted octahedral FePt nanoparticles on a substrate through sputtering has been reported by Shima et al. [35]; these particles were slightly larger (about 20 nm) because they were to be applied for magnetic materials. It was also expected that FePt nanoparticles possess high thermal stability (that is necessary for the synthesis of CNT forest) because of the repetition of thin-film deposition and heat treatment at high temperature.

In this paper, we report the fabrication of {1 1 1}-faceted FePt particles on a single-crystal MgO substrate and the synthesis of SWCNT forests using these faceted particles on the substrate. For the first time, we have successfully prepared faceted FePt nanoparticles having high thermal stability, and synthesized SWCNT forests with a metallic chiral structure on the substrate.

2. Experimental

2.1. *Preparation of FePt films*

All FePt layers were fabricated using an ultra-high vacuum (UHV) magnetron sputtering system (MPS-2000-C8, ULVAC Inc., Japan). Table 1 shows a representative condition for sputtering deposition of FePt/MgO films.

A single crystalline MgO(0 0 1) substrate (Tateho Chemical Industries Co., Ltd., Japan) was selected for reasons similar to those described in previous reports [35,36]; in particular, a lattice mismatch between MgO and FePt (because a lattice parameter of MgO is slightly larger than that of FePt) is expected to induce epitaxial growth of FePt. Good chemical stability and high melting point of MgO are additional benefits. To clean substrate surfaces, MgO substrates were heated up to 1013 K for 1 h in a UHV chamber. The films in this study were prepared by alternate deposition of FePt and MgO layers. The substrates were heated up to 1013 K for depositing FePt layers and then cooled to room temperature (R.T.) for the deposition of MgO layers. Layer compositions and thicknesses were FePt (0.25–1 nm)/[MgO(0.5–1 nm)/FePt(0.25–1 nm)]$_X$ (where $X = 1$ or 2); total thicknesses of FePt layers were between 0.75 and 3 nm. These thicknesses differed on the

Table 1 – Sputtering conditions for preparing catalytic substrates.

Target (at.%)	Fe (99.99), Pt (99.9), MgO (99)
Base pressure (Pa)	$<1.0 \times 10^{-8}$
Working pressure (Pa)	0.13
Input power (W)	Fe (19/DC), Pt (15/RF), MgO (108/RF)
Substrate temperature	Fe, Pt: 1013 K, MgO: R.T.
Sputtering rate (nm/s)	Fe: 0.01, Pt: 0.01, MgO: 0.003