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Utilization of catalyst deactivation for the growth of aligned and random carbon nanotubes by a single-step process

Sangeeta Handuja, P. Srivastava *, V.D. Vankar

Nanostech Laboratory, Department of Physics, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India

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ABSTRACT

We have synthesized hybrid carbon nanotubes (CNTs) i.e. random secondary carbon nanotubes, on top of the aligned primary CNTs grown on Fe deposited n-type (1 1 1) silicon substrate by thermal chemical vapor deposition technique utilizing the concept of catalyst deactivation. The transmission electron microscopy and Raman spectroscopy results reveal that the primary CNTs are highly pure and crystalline and the secondary CNTs contain defects and impurities with a low degree of crystallinity. It is observed that by providing Fe catalyst during deposition, vertically aligned primary CNTs are synthesized for a shorter duration of growth. Random and entangled secondary CNTs on top of primary tubes are found to grow if the duration of growth is increased. It is suggested that termination of primary CNTs after a short time duration is because of the deactivation of the Fe catalyst deposited on the substrate, whereas Fe catalyst provided in the precursor solution initiates secondary growth of CNTs. The present work also suggests that base and tip growth mechanisms are responsible for the growth of primary and secondary CNTs, respectively.

1. Introduction

Carbon nanotubes (CNTs), known for their considerable potential in diverse applications such as in field emission [1–7], nano electronics [8] and energy storage (supercapacitors and hydrogen storage) [9,10] devices, can be synthesized by different techniques like arc discharge [11,12], laser ablation [13] and chemical vapor deposition (CVD) [1–10]. Among these techniques, thermal chemical vapor deposition (T-CVD) has emerged as an efficient technique for large-scale production of CNTs on various substrates such as silicon, copper, alumina, quartz and nickel [14,15]. It is well established that the morphology of the CNTs affects some of their important properties, e.g. randomly oriented CNTs show excellent field emission because of the existence of numerous defects [2,5,6], and vertically aligned CNTs exhibit high current reliability and low operating electric field [1,3]. The electrochemical properties of CNT-based supercapacitors also depend on the morphology of the CNTs as the surface area provided by aligned and random CNTs differs significantly [9,16]. Therefore, it is important to have a control over the growth mechanism responsible for morphology of CNTs, especially on silicon, as it is widely used in the semiconductor industry. The T-CVD technique has been successfully used for the synthesis of CNTs with a control on their alignment and density. Many groups have reported the growth of several layers of CNTs on various substrates such as silicon, quartz and multi-layers of Fe/Al and Ni/Al catalysts [17–24]. Sun et al. [17] reported the growth of aligned CNTs on the already existing array of CNTs by oxidizing the first array in air and then reducing it in a hydrogen environment. Layered growth of well-aligned arrays of multi-walled CNTs (MWNTs) separated by Fe catalyst particles was studied by Liu et al. [18] and they reported that the morphologies of layered growth depend on the catalyst pre-treatment. Deck and Vecchio [19] found that varying the time interval between the introductions of solution formed well-aligned layers of CNTs. Zhang et al. [20] reported the layered growth of aligned CNT arrays on quartz using Co powder and showed that the length of CNTs varies as a function of temperature. It has also been reported that the CNT growth is eventually limited by the deactivation of the catalyst [25,26]. Eres et al. [21] partially overcame the problem of catalyst deactivation by providing additional Fe catalyst in gas stream during a typical CVD process. In situ growth of secondary CNTs known as carbon nanotubules during the growth of vertically aligned CNTs has also been observed by fragmentation of Ni catalyst at deposition temperature by plasma-enhanced CVD (PECVD) [22]. Synthesis of hybrid MWNTs (aligned and random combination) on glass substrate has also

* Corresponding author. Tel.: +91 11 2659 6558; fax: +91 11 2658 1114.
E-mail addresses: pankajs@physics.iitd.ernet.in, pankaj_17_66@yahoo.com (P. Srivastava).

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been reported by Kim et al. [27] by consecutive growth with PECVD and T-CVD. Regrowth of CNT arrays has also been studied by using a combined system of plasma-enhanced thermal CVD and microwave-plasma-enhanced CVD [28].

The growth of secondary CNTs on top of the primary CNTs can modify some of the properties of the latter, e.g. enhancement in specific surface area has been reported by growing secondary CNTs after electro-deposition of Fe particles and by attaching nickel particles on the primary CNTs [23,24]. It is also observed that by depositing a metal catalyst on the surface of thick CNT layer, growth of thin secondary CNTs gives field emission uniformity [6,29].

In the present work, we report a method of efficient growth of hybrid CNTs, i.e. vertically aligned as well as random CNTs by T-CVD. Iron was deposited on silicon substrate prior to CNT deposition and was also provided with the precursor solution. Unlike earlier reports, we have used a single-step process (i.e. T-CVD) without further catalyst deposition for secondary growth after the growth of primary CNTs. This provides considerable control over the length of primary CNTs as well as the density of secondary CNTs. The effect of duration of growth on the growth mechanism of secondary CNTs by providing in situ Fe catalyst has also been studied.

2. Experimental details

A Fe film of ~20 nm thickness was deposited on n-type silicon (111) wafers using thermal evaporation. Heat pre-treatment to this Fe-coated silicon was carried out in the CVD chamber used for CNTs growth in argon ambient at 880 °C for 20 min. These Fe-deposited Si wafers were subsequently used as substrates for CNT growth by T-CVD. The experimental set-up used for the growth of CNTs by T-CVD has been described elsewhere [30]. The substrate was placed on a quartz boat, which was in turn loaded into a quartz reaction tube (14 mm inner diameter and 90 cm in length) located in a tube furnace of 25.4 mm diameter. Prior to CVD growth of CNTs, the quartz tube was purged by Ar gas. A solution of ferrocene in xylene of 0.02 gm/ml concentration was then sprayed with a glass sprayer. For this set-up the optimum growth temperature for CNTs was found to be 880 °C. The CNT growth was investigated at different active durations of growth during the CVD process ranging from 50 to 200 s while keeping other growth parameters constant.

Size distribution of Fe catalyst particle on the silicon wafer was analyzed using atomic force microscope [Nanoscope IIIa (Veeco Metrology Group)] in contact mode. The surface morphology, cross-section and growth behavior of the CNT samples were analyzed by a scanning electron microscope (SEM: Stereo scan 360) operated at 15 kV. The microstructures of the samples were analyzed by a transmission electron microscope (TEM: Phillips CM 12) and high-resolution transmission electron microscope (HRTEM: Technai G2, EDAX company USA) operated at 100 and 200 kV, respectively. For TEM and HRTEM, samples were scratched from silicon substrates using a tweezer, then refluxed and ultrasonicated in ethanol to disperse, then transferred onto a carbon-coated copper grid. Raman spectra of the samples were recorded using a micro-Raman spectrometer model T 64,000 with Argon laser of excitation wavelength 514.5 nm at 50 mW power and 2 μm probe diameter.

3. Results and discussion

The AFM image of the silicon substrate after pre-heat treatment is shown in Fig. 1. Pre-heat treatment of the substrate resulted in the splitting of Fe film into nanoparticles of Fe on the substrate. The inset of Fig. 1 shows the histogram of average particle size distribution of the Fe nanoparticles as calculated from analysis of AFM images. Average particle size distribution of the Fe nanoparticles is around 100–200 nm with a standard deviation of 40 nm.

The growth of CNTs over the pretreated substrate commences immediately after the process of spraying of precursor starts. We studied the change in morphology and microstructure of CNTs grown for durations of 50, 90, 100, 130, 190 and 200 s. Fig. 2 shows the low- and high-magnification SEM images of these CNT samples. Fig. 2(a) shows the cross-section of a sample grown for 50 s with an arrow indicating the direction of alignment in these CNTs. The average length of these CNTs as measured from the cross-section of the sample is around ~18 μm. As shown in Fig. 2(b), the length of aligned CNTs increases to ~25 μm by increasing the duration of growth from 50 to 90 s. It has been widely reported that the growth of CNTs is a function of diameter and density of the catalyst [31]. However, with increase in the duration of growth, it is noticed (Fig. 2(b)) that at some points the growth saturates (shown by horizontal arrow) whereas at some other positions it is still in progress (vertical arrow). By further increasing the duration of growth to 100 s (Fig. 2(c)), the length of CNTs does not increase further and also the growth process of primary CNTs comes close to termination. However, initiation of growth of a different morphology (arrow in Fig. 2(c)) of CNTs known as secondary growth starts, which progresses with time till 130 s (Fig. 2(d)) while the inset of Fig. 2(d) shows that the aligned nature of primary CNTs is still maintained. Fig. 2(e) shows the surface micrograph of the sample grown for a duration of 190 s, indicating the denser growth of secondary CNTs. A high-magnification SEM image of these secondary CNTs (left inset of Fig. 2(e)) indicates that they are random in nature. The vertical cross-sectional image of the same sample (right inset of Fig. 2(e)) shows that primary CNTs continue to be vertically aligned. For a growth period of 200 s, the top layer of primary CNTs is completely covered with secondary CNTs (Fig. 2(f)). However, as shown in the high-magnification image of the secondary CNTs grown for 200 s (left inset of Fig. 2(f)), secondary CNTs become more and more random and coiled as growth process is continued for a longer duration. The cross-sectional micrograph of the same sample as shown in the right inset of Fig. 2(f) is similar to that of

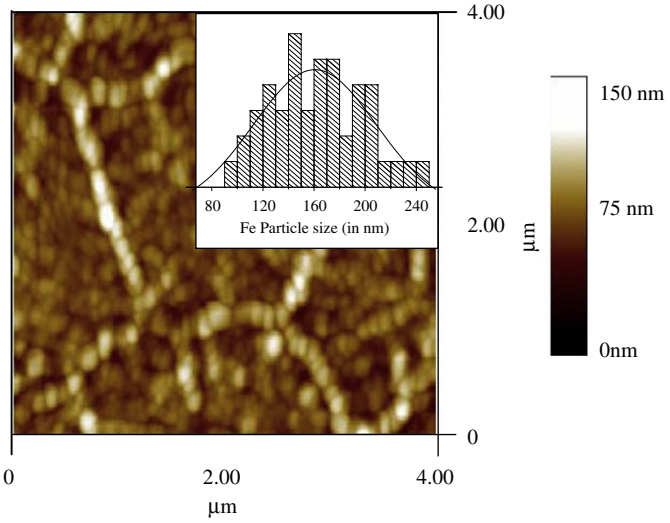

Fig. 1. AFM image of surface of silicon substrate with Fe catalyst after heat treatment. Inset shows the histogram of the catalyst particle size distribution.