LOW-TEMPERATURE, NONLINEAR FAST GROWTH OF ALIGNED CARBON NANOTUBES WITH HIGH AREA-DENSITIES

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Introduction

Carbon nanotube (CNT) and carbon nanowire (CNW) represent two types of one-dimensional nanocarbons. Between them, CNT has received much more attention in the past. A number of methods have been used for the growth of CNT. Among them, the microwave plasma-enhanced chemical vapor deposition (MPCVD) method provides an advantage for carbon nanotube growth at relatively lower temperatures [1,2] and is therefore commonly used. Regardless of the growth techniques, a catalyst is normally required. Typical catalysts include Ni, Co, and Fe transition metals, even Co/Ni, Fe/Ni, and Y/Ni mixture, and Fe-Ni and Y-Ni alloys. It is known that the nature and the preparation of catalyst significantly influence the growth and characteristics of CNTs, although the complete mechanism has not been determined. On the other hand, CNW was synthesized using a thermal evaporation technique in the presence of crystalline Ni catalyst [3] and a thermal annealing technique to convert SiC film into nanowire [4]. As in CNT, a catalyst is required. However, the role of the catalyst characteristics on the formation of CNW has not been well-examined. We report in the paper that by proper selection and treatment of catalysts one can obtained either CNT or CNW. Furthermore, we report low-temperature, nonlinear fast growth of aligned CNTs with high area-densities.

Experimental

Thin films of Ni, Fe, and FeSi alloy were used as the catalysts for carbon nanowire or nanotube growth. The thin film catalysts were deposited on silicon substrates using a magnetron sputter deposition technique. CNWs or CNTs were then grown in a microwave plasma-enhanced chemical vapor deposition system under a CH_4 and H_2 gas mixture. The growth temperature was determined to be 450℃. Prior to the growth, thin film catalyst were etched for 5 min under hydrogen plasma. Specimens of thin film catalyst, CNWs, and CNTs were analyzed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), micro-Raman spectroscopy, and x-ray diffractometry (XRD). To determine the area-density (no. of CNTs/cm^2), CNT specimens were infiltrated with epoxy. After cuing the epoxy, CNT/epoxy was removed from the silicon substrate. The surface of CNT/epoxy, which was in contact with the silicon substrate before the removal, was examined using SEM for counting the number of CNTs.

Results and Discussion

Three different types of catalysts have been used to grow one-dimensional nanocarbons. The use of amorphous Ni led to the formation of aligned CNW as shown in Fig. 1A. The growth time is 3 minutes and the height is approximately 400 nm, which give a growth rate of 133 nm/min. The diameters of nanowires were found to be quite uniform, with an aveage of 40 nm. The solid nature of CNW is shown in Fig. 1B. This figure also shows a catalyst particle at the tip of the CNW. Unlike other CNWs [5-7], the CNWs exhibit a polycrystalline structure, according to selected area diffraction patterns. The catalyst at the tip was determined to be a NiC particle with $L1_0$ structure [7]. CNW specimen was also examined using micro-Raman spectroscopy, as shown in Fig. 1C. The Raman signatures consist of two peaks near 1322 cm^{-1} (D-band) and 1578 cm^{-1} (G-band), similar to that of carbon nanotubes. The G-band corresponds to a phonon high-frequency E_{2g} first-order mode of graphite and is related to the vibration of sp^2-bonded carbon atoms in a two-dimensional hexagonal lattice, such as in a graphite layer [8-10]. The D-band is associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite [8], defects in the curved grapheme sheets, and the turbostratic structure of grapheme structure in the materials. It is noted that in Fig. 1C that the D-band peak is quite significant. This indicates that two-dimensional disorders exist in the basal plane which is quite common in pyrolytic carbon materials synthesized using MPCVD [8]. In addition, A shoulder peak D'-line at ~1600 cm^{-1} is induced by disorders resulting from the finite size effect or lattice distortion [9,10]. We also found that G-band peak broadening was greater than 60 cm^{-1} and the I_D/I_G ratio decreased with FWHM similar to that for a-C:H. This indicated that the D-band structure of CNWs is dominated primarily by smaller aromatic clusters with cluster sizes smaller than 1 nm.

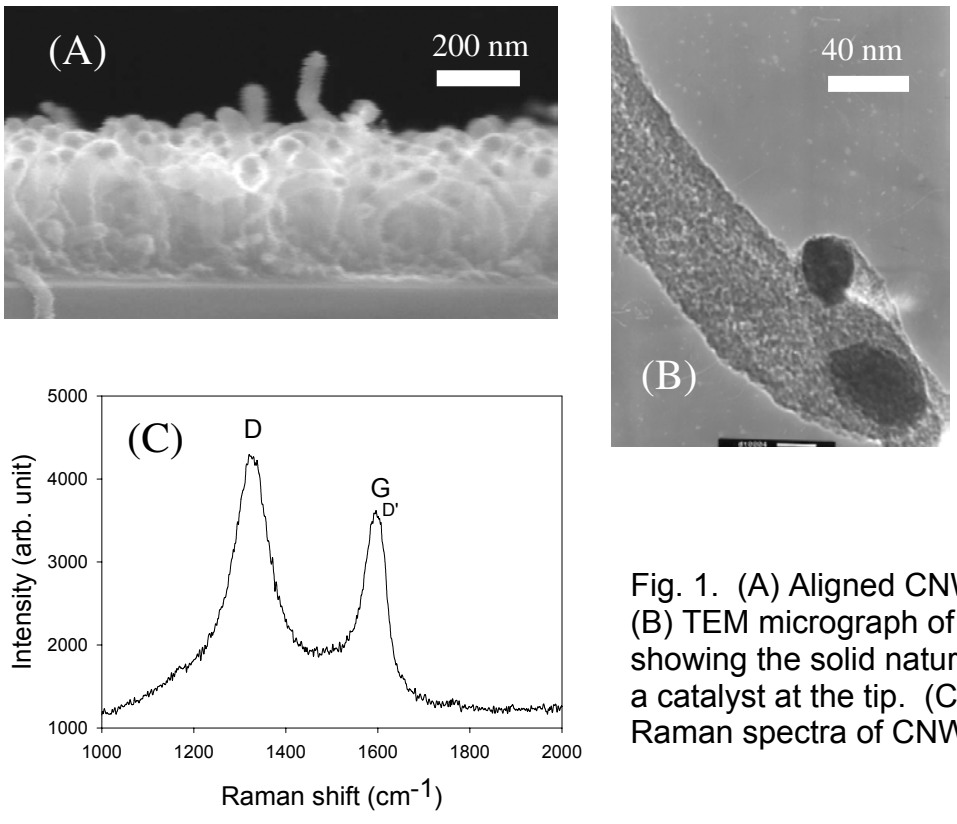

Fig. 1. (A) Aligned CNWs. (B) TEM micrograph of CNW showing the solid nature and a catalyst at the tip. (C) Raman spectra of CNW.

When Fe was used as the catalyst, only rock-like carbonaceous clusters were obtained. This is shown in Fig. 2. However, when amorphous FeSi was used as the catalyst, fast, nonlinear growth of well-aligned CNTs with high area-density was observed. Fig. 3 shows aligned CNTs obtained at power of 500 W, CH_4/H_2 ratio of 2/9, a growth time of 4 min, and a growth temperature of 450℃. It appears that CNTs not only are well-aligned but also have a very high area-density, which was estimated to be higher than 10^{10}. The growth of CNTs was found to follow the root-growth model. It was also found that the diameters were almost unchanged with time. At a CH_4/H_2 ratio of 2/9, the average diameter for all CNTs obtained is 12±1 nm. This indicates that the growth kinetics of CNT can be represented by the lengthening rate. Under a CH_4/H_2 ratio of 2/9, CNTs were not observed until the synthesis time reached 45 seconds. The 45-second CNT has a length of 0.44 μm. When the CNT length, L, was plotted as a function of the growth time, t, an unprecedented nonlinear growth behavior was found. The growth rate increases with time. For CNTs obtained a CH_4/H_2 ratio of 2/9, the growth kinetics is shown in Fig. 4. The highest growth obtained is 13 μm/min obtained at a CH_4/H_2 ratio of 4/9, which is higher than most of the reported values and the highest among all the low-temperature growth. The fast, nonlinear growth rate and the high area-density are attributed to the high diffusivity of carbon in FeSi and the ability of amorphous FeSi to form a tremendous amount of nanoparticles (less than 5 nm) after etching. It is noted that the diffusivity of carbon in Fe can be varied in the presence of Si. The diffusivity of carbon in austenitic steels is reduced by the presence of Si when the carbon concentration is low or near the solubility limit as well as at high temperatures [11]. However, at higher carbon concentrations the diffusivity of carbon is actually increases in the presence of Si [12]. This is especially true when one compares carbon diffusivity in pure Fe and in Fe-Si-C. For example, at a temperature of 500℃, the carbon diffusivity in Fe-Si-C is 10 times higher than that in Fe. In this study, the carbon concentration can be as high as 12 atomic % [13].

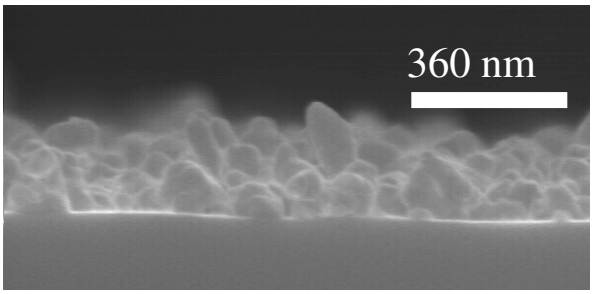

Fig. 2. SEM image shows that carbonaceous clusters was synthesized using pure Fe film as a catalyst under 500 W, CH_4/H_2 = 2/9 and 25 Torr for 3 min.

Conclusion

In this study, we have obtained crystalline carbon nanowires using amorphous Ni thin films as the catalysts. The Raman signatures indicate that the structure of CNW is dominated by smaller aromatic clusters with cluster sizes smaller than 1 nm and similar to that for a-C:H. On the other hand, when amorphous Fe-Si alloy was used as the catalyst, fast, nonlinear growth of well-aligned CNTs with high area-density was

observed. The highest growth obtained is 13 μm/min obtained at a CH_4/H_2 ratio of 4/9, which is higher than most of the reported values and the highest among all the low-temperature growth. This is attributed to the high diffusivity of carbon in FeSi and the ability of amorphous FeSi alloy to form a tremendous amount of nanoparticles (less than 5 nm) after etching.

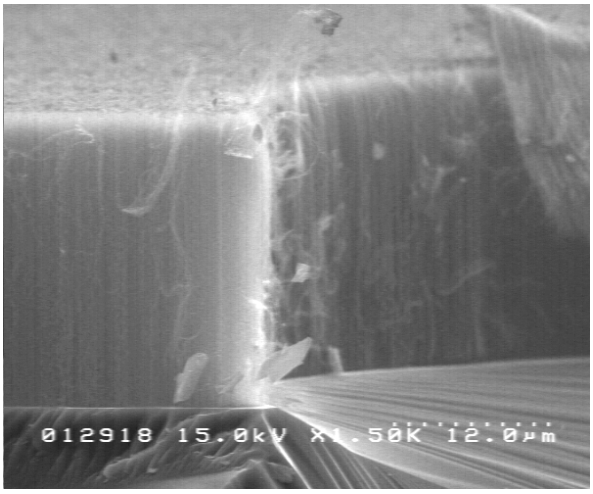

Fig. 3. An SEM image showing cross-sectional view of high-density aligned carbon nanotubes grown on Fe-Si.

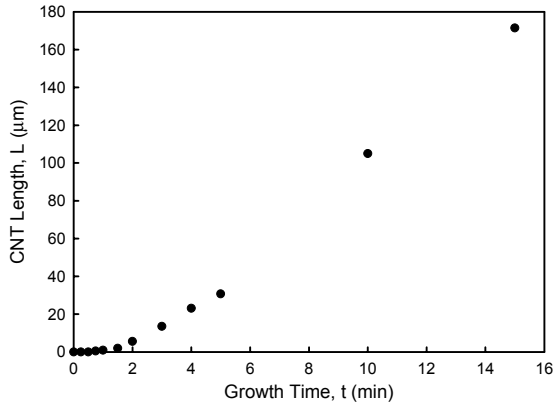

Fig. 4. CNT length as a function of time.

Acknowledgement

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