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Very rapid growth of aligned carbon nanotubes on metallic substrates

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Abstract

Aligned carbon nanotubes were grown on metallic substrates using a microwave plasma-enhanced chemical vapor deposition system. The substrates were Ni and Cu, and the catalyst was an Fe–Si alloy thin film. The effects of substrate and catalyst characteristics and growth temperature were studied. We show, via the use of a microwave shield, and with optimized catalyst thickness and growth temperature, that carbon nanotubes (CNTs) with a length of up to 2.15 mm and an unprecedently high growth rate of 177 μm min^{-1} can obtained. Non-isothermal growth was performed to investigate the growth kinetics and therefore to obtain the activation energies of CNTs grown on Ni and Cu. Very similar activation energies for the growth of CNTs on Ni and Cu substrates were determined to be 101.5 (1.05 eV) kJ mol^{-1} and 102.3 (1.06 eV) kJ mol^{-1}, respectively.

Keywords: Carbon nanotubes; Metallic substrates; Microwave plasma-enhanced chemical vapor deposition; Activation energies

1. Introduction

The growth of aligned carbon nanotubes (CNTs) requires the use of a substrate that includes non-conducting quartz, a semiconducting silicon wafer and a conducting metal [1–15]. Aligned CNTs grown on conducting metal substrates have been shown to exhibit characteristics that are desirable for applications in field emission [9,10,15] and supercapacitors [10–14]. For such applications, the aligned CNTs must be in intimate contact with the conducting substrate to ensure not only mechanical integrity but also low contact resistance between them. For example, it has been shown that electrodes consisting of aligned CNTs grown on metal current collectors not only avoid the use of a conductive binder but also decrease the electric contact resistance between the aligned CNTs and the current collector [14].

The growth of aligned CNTs on metallic substrates has been reported using a number of thermal chemical vapor deposition (CVD) techniques [9–11,16–19]. The growth temperatures reported were between 550 and 800 °C, which, however, gives only single-digit growth rates (μm min^{-1}) or less. Water-assisted CVD growth at 800 °C gives a growth rate of ~20 μm min^{-1} on bilayer Al/Fe coated stainless steel [20]. CNTs have also been grown on metallic substrates using non-thermal CVD methods, involving the use of plasma [21–25]. Although the growth temperatures are lower, typically around or less than 600 °C, the use of plasma still fails to boost the growth rate or length when a metallic substrate is used. The resulting growth rates are poor, ranging from 0.08 to 20 μm min^{-1}. This is apparently due to the very undesirable interactions between plasma and metals. Such reflected loss must have severely hindered the deposition of the growth species onto the substrate, leading to very limited growth, if any. Also, the reflection loss increases with the electrical conductivity of the metal [26]. To avoid such interactions, it is believed that the use of a microwave shield could prevent the reflection of microwaves from metallic substrates.

The shielding effectiveness (SE) of a material can be expressed by the following equation:

$$SE = SE_a + SE_r + SE_m \quad (1)$$

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where SE_a is the absorption loss, SE_r is the reflection loss and SE_m is multiple reflection losses [27]. The multiple reflection losses that occur when the shield has a large surface or interface area is not considered here. The values of SE_r and SE_a can be estimated using the following equations [28]:

$$SE_r = 39.5 + 10\log\left(\frac{\sigma}{2\pi f \mu_p}\right) \quad (2)$$

$$SE_a = 8.7\left(\frac{t}{\delta}\right) \quad (3)$$

where σ, f, μ_p, t and δ are the electrical conductivity, plasma frequency, magnetic permeability, thickness of the shield and skin depth of the shield, respectively. The value of δ can be obtained using the following equation:

$$\delta = \frac{1}{\sqrt{\pi f \sigma \mu_p}} \quad (4)$$

As a result, when a 0.5 mm thick Si coupon is used as the shield, there is nearly no reflection and the value of SE_a is at least 20 dB, giving attenuation of microwaves down to less than 1%. This approach has been demonstrated previously for the microwave plasma enhanced (MPE) CVD growth of aligned multi-walled CNTs on Ni and Cu substrates, at excellent growth rates of 62 and 25 μm min^{-1}, respectively [15]. The growth temperatures were ~600 °C.

Similar approaches have been reported for the growth of single- and double-walled CNTs on Si substrates, which were partially covered using an Si coupon [29]. The growth temperature was 850 °C; however, the growth rates were low (7.2–12 μm min^{-1}). In this study, we show that the growth can be further enhanced by reducing the thickness of the catalyst layer or just slightly increasing the growth temperature. An unprecedently high growth rate of 177 μm min^{-1} was obtained. As a result, the growth kinetics and activation energy were determined. This was done by non-isothermal growth. Non-isothermal growth can be achieved in an MPECVD chamber since a substrate can be heated by the microwave radiation without an external heating source. The microwave heating occurs gradually so that the substrate temperature increases with growth time before reaching a saturated temperature. The substrate temperature was also varied by placing the substrate at different locations within the microwave plasma ball. The growth kinetics of CNTs was thus studied under different temperatures. This allows the determination of the activation energy required for CNT growth on metallic substrates.

2. Experimental

Ni and Cu coupons were used as the substrates for the growth of CNTs in an MPECVD system. The catalyst used was an Fe–Si thin film catalyst prepared using co-sputter deposition at a power of 50 W and an Ar pressure of 1×10^{-2} torr. The deposition time was varied from 15 to 60 s in order to obtain Fe–Si thin films with different thicknesses. The Fe–Si catalyst thus prepared has a composition of 21 at.% Si and 79 at.% Fe and results in a root-growth mode for the CNTs [15]. Selected substrates were predeposited with an 8 nm Al underlayer, also by sputter deposition. Prior to the CNT growth, the catalyst-deposited substrates were etched under 20 torr of H_2 plasma for 5 min to change the catalyst film into particles, which are the nucleation sites for the growth of CNTs. Since the H_2 plasma treatment time affects the formation and size of the particles, the etching time of 5 min was predetermined. During the H_2 plasma treatment, the substrate temperature increased from 200 to 450 °C. At the end of the plasma treatment, the substrate was allowed to cool down to room temperature under H_2 gas before the introduction of CH_4 for the growth of CNTs. The growth of CNTs then took place under a methane/hydrogen mixture of 30.7%, a microwave power of 400 W and a pressure of 40 torr. The growth time was varied between 0 and 20 min. During the growth of the CNTs, a 0.5 mm thick Si coupon was used as a shield, which was placed 2 mm above the substrate. The placement of the Si coupon was such that the supply of the C source to the substrate was not affected. The substrate was then heated gradually by microwave radiation. The substrate temperature was constantly monitored using a optical pyrometer, starting at the initial time of growth. In order to grow CNTs at different temperatures, the substrate was placed at two different locations: one at the bottom of the microwave plasma and the other in the middle. The resulting CNTs were analyzed for length and microstructure using scanning electron microscopy (SEM; EEISS, Auriga 39–50).

3. Results and discussion

As mentioned above, due to microwave reflection, the growth of CNTs is extremely slow – typically less than 1 μm min^{-1} under all the microwave conditions without the use of a shield. Significant growth enhancement was obtained when a shield was used. The enhancement was found to depend on both the catalyst thickness and the growth temperature.

The effect of catalyst thickness is first presented. Fig. 1 shows SEM images of CNTs grown on Ni substrates using different catalyst thicknesses (2, 4, 8 and 40 nm). The growth time was 10 min. As shown in Fig. 1, the growth increases from the 2 nm sample to the 4 nm one. The growth then decreases when the catalyst's thickness exceeds 4 nm (see e.g. the 8 and 40 nm samples shown in Fig. 1C and D, respectively). Similar results showing that the growth peaks at a certain catalyst thickness have been reported elsewhere [30,31]. However, the mechanism is currently unknown. The length limit depends on the thickness of the Fe–Si catalyst. It increases then decreases with the catalyst thickness. In this study, the maximum CNT length