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Sandwich Growth of Aligned Carbon Nanotubes Array using Thermal Chemical Vapor Deposition Method

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Abstract: Production of highly oriented Carbon Nanotubes (CNTs) array is desirable when enhanced electrical properties are required for better performed nanotubes-based devices. The conventional method produces single array CNTs which does not fulfil the requirement for two terminal devices. The study reports a successful production of double layer structure of aligned carbon nanotubes array as a result of the sandwich growth via thermal Chemical Vapor Deposition (CVD) method. Unlike the reported microwave plasma CVD method which uses a tiny top substrate, the high density aligned multiwalled CNTs grown here are from equal-sized catalyst coated substrates stacked in the sandwich configuration. This proves that thermal CVD method is capable of producing good quality, freestanding CNTs array that are connected to two surfaces for possible application in the two terminals electronic devices.

Key words: Carbon nanotubes, catalyst, chemical vapor deposition, sandwich configuration, buffer layer

INTRODUCTION

Production of good quality, clean and highly oriented CNTs array is critical for functional devices such as scanning probe and sensors (Dai *et al*., 1996; Wong *et al*., 1998; Modi *et al*., 2003) and field emitters (De Deer *et al*., 1995; Collins and Zettl, 1996; Wang *et al*., 1997; Wang *et al*., 1998; Bonard *et al*., 1998). As such, an effort is required to grow nanotubes in a ready-made structure without manipulation or assembly for construction into a useful device structure. Formation of freestanding, small diameter carbon nanotubes had been reported using microwave plasma chemical vapor deposition (Lai *et al*., 2008). Driven by the need to create nanotube-based two terminal sensors, a similar study had been carried out here using thermal CVD method instead. This method used Fe catalyst and ethylene as carbon feedstock. The wafer was first deposited with Al followed by oxidization to form buffer layer. Having Al_2O_3 underneath Fe layer would improve the alignment and density of the CNT growth (Lai *et al*., 2008; De Los Arcos *et al*., 2004). Three different configurations of the wafer stacking are studied namely with catalyst on top wafer, on bottom wafer and on both wafers. The CNTs obtained are analyzed using Raman spectroscopy and scanning and transmission electron microscopy. Results obtained are compared with the conventional method which had been proven to produce good quality vertically aligned CNTs film (Lai *et al*., 2008).

MATERIALS AND METHODS

Cleaned Si wafers of 4 cm^2 size were deposited with fresh layer of 300 nm SiO_2, followed by Al_2O_3 buffer layer and final coating of Fe catalyst (Lai *et al*., 2008). The buffer layer was found to play an important role in producing well-aligned CNT film (Lai *et al*., 2008, De Los Arcos *et al*., 2003, 2004). The two equal size substrates are stacked such that the coated surfaces are in contact with each other in three different configurations shown in Fig. 1:

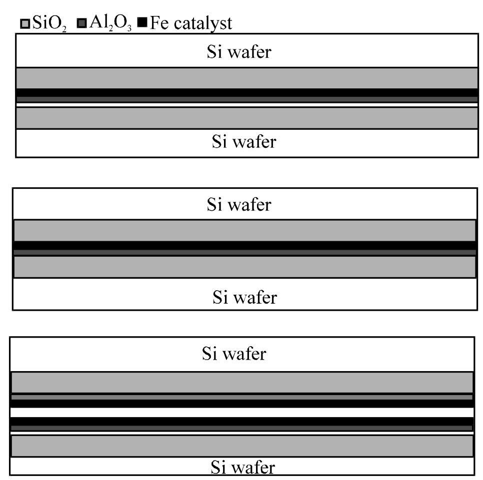

Fig. 1: Sandwich stacking for 3 samples

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- Sample 1-Both substrates are coated with SiO_2, buffer layer and catalyst
- Sample 2-Top substrate has SiO_2, buffer layer and catalyst layer whereas the bottom substrate consists of SiO_2 only
- Sample 3-Bottom substrate has SiO_2, buffer layer and catalyst layer whereas the top substrate consists of SiO_2 only

At the same time, the growth of CNTs using the conventional, single substrate method was also carried out in order to compare and investigate the effect of the stacking configuration on the grown CNTs. This conventional method had been proven (Lai *et al*., 2008) to produce vertically aligned, good quality CNTs.

Figure 2 outlines the conventional and sandwich growth of nanotubes investigated here. As in the conventional sample (Fig. 2a), the catalyst layer is deposited onto the only substrate. With the sandwich type that has 2 substrates, only the top substrate as in sample 1 in Fig. 2b and the bottom substrate as in sample 2 in Fig. 2c will be coated with the catalyst. As for sample 3 in Fig. 2d both substrates will be deposited with the catalyst layer. Since the top and the bottom substrate of the sandwich type are of the same size and placed together with no air gap, carbon excess to the catalyst is only at the sides.

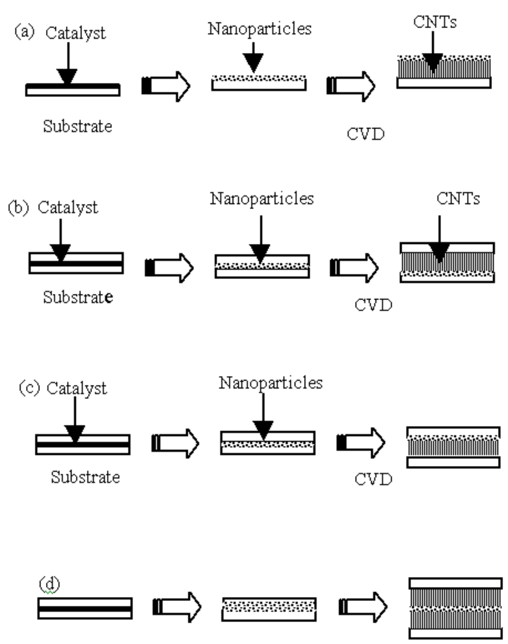

Fig. 2: Conventional and sandwich growth of vertically aligned CNTs by thermal CVD method; (a) Conventional sample, (b) Sample 1: sandwich type with catalyst coated top substrate, (c) Sample 2: sandwich type with catalyst coated bottom substrate and (d) Sample 3: sandwich type with catalyst coated top and bottom substrate

RESULTS AND DISCUSSION

CNTs films have been successfully produced via the sandwich method. As described in Fig. 2, a single layer of CNTs film was obtained for the conventional type and the sandwich type of sample 1 and 2. For sample 3 which is the sandwich type with top and bottom substrate coated with catalyst, a double layer of CNTs film was grown. For SEM analysis, the top substrate of the sandwich type was carefully removed.

Upon removal, CNT film was found to remain intact with no noticeable amount of CNTs sticking onto the other substrate. SEM image of vertically aligned forest of CNTs for sample 1, 2 and 3 are shown in Fig. 3. The height of CNTs forest was found to be in the range of 27 to 32 μm.

EDX carried out on the surface had identified the particles on the tips of nanotubes in both substrates of sample 3 to be amorphous carbon (Fig. 4) whereas particles found on nanotubes in Sample 1 and Sample 2 contain some traces of Fe, probably an indication of tip growth.

The presence of amorphous carbon in sample 3 could be due to the ineffective removal by H_2 from the close-up region between two substrates as CNTs are growing from both substrates. It should be pointed out that in the above growth process; H_2 continues to be purged into the furnace upon termination of CNT growth for the purpose of removing amorphous carbon and producing cleaner nanotubes. Cleaner CNTs films for direct application in electronic devices are preferred because any post treatment for purification could disrupt the vertical alignment and possibly remove nanotubes entirely from the substrate.

Unlike what has been reported by Chen *et al*. (2006) where catalyst nanoparticles are found midway between the cover and substrate, the evidence obtained here for sample 1 and sample 2 shows that the catalyst nanoparticles are located at the tips of the nanotubes, indicating the tip growth mechanism. The difference is that Chen *et al*. (2006) used plasma CVD method with the much smaller size top cover and a tiny gap in between the cover and the bottom substrate. Here, CVD method is adopted to grow nanotubes from equal size and weight of substrates placed on top of each other without any gap.

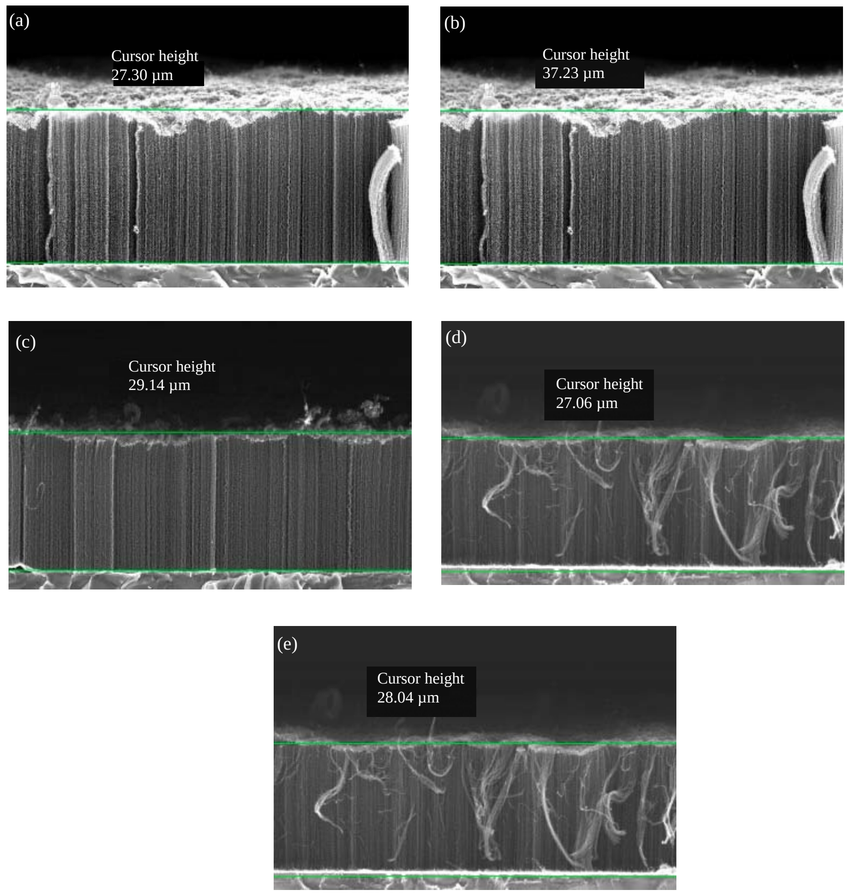

Fig. 3: SEM images of (a, b, c and d) sandwich type samples and (e) conventional type sample; (a) Sample 1: catalyst coated top substrate, (b) Sample 2: catalyst coated bottom substrate, (c) Catalyst coated top substrate of sample 3, (d) Catalyst coated bottom substrate of sample 3 and (e) Catalyst coated bottom substrate of conventional type

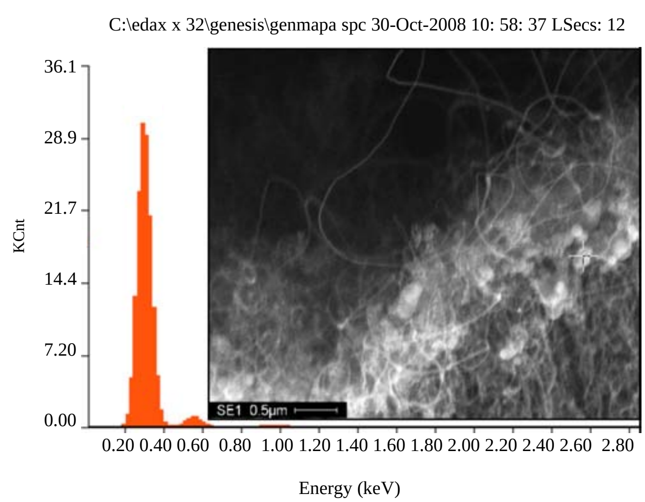

Fig. 4: EDX on particles at the tips of CNTs with the inset showing the SEM image of the surface of CNTs film

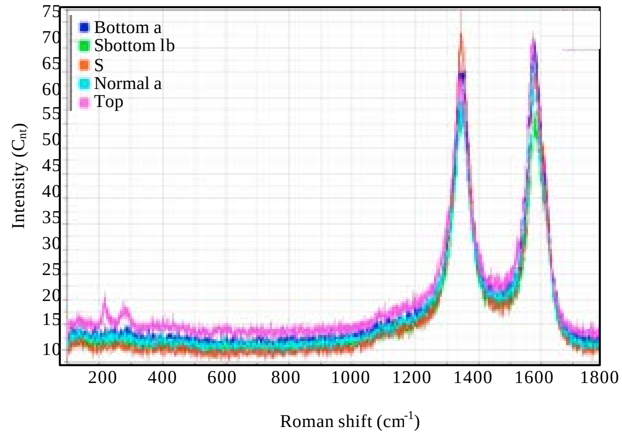

Fig. 5: Raman spectra for sample 1 (top and bottom substrate), sample 2 (top substrate) and sample 3 (bottom substrate)

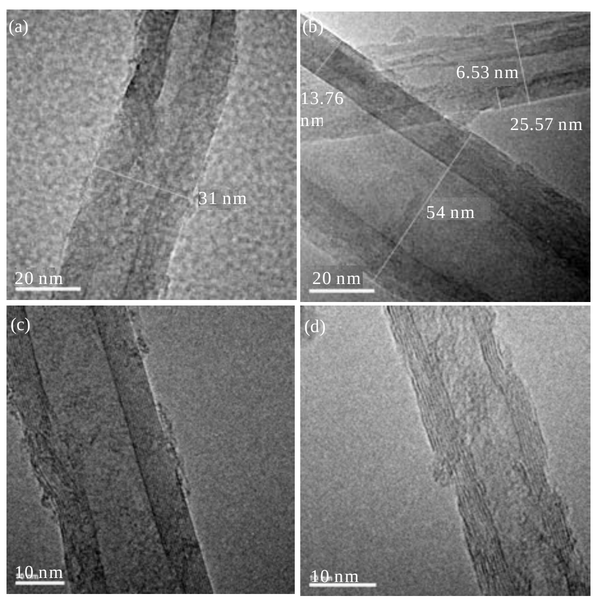

Fig. 6: TEM images of multiwalled nanotubes grown by sandwich configuration for (a) bottom, (b) top catalyst coated substrate only, (c) bottom and (d) top of both substrates coated with catalyst

As evidence in Fig. 4, the growth of nanotubes originates from nanoparticles deposited on the each substrate such that for both catalyst coated substrates in sample 3, a double layer structure of nanotubes was obtained. The vertical alignment and density of nanotubes obtained with sandwich type are observed to be comparable to the conventional type (Fig. 3e). This significant finding implies that the catalyst film may not necessarily be exposed directly to the hydrocarbon feedstock in order for the CNTs to grow. The CNTs film also does not exhibit any buckling or bending as a result of the weight of the top substrate which is of equal weight and size with the bottom substrate, demonstrating the high strength of the CNTs.

The samples were analyzed by Raman spectroscopy, giving the spectra shown in Fig. 5. CNTs films grown from both catalyst coated substrates have shown higher I_D/I_G ratio (both substrates of sample 1~1.04), than the ones grown from the single catalyst coated substrates (Sample 2 and 3~0.9), implying lower crystallinity.

The result of lower crystallinity exhibited by CNTs grown from sandwich type with both top and bottom substrates coated with catalyst is supported by the observation made on the TEM images shown in Fig. 6c and 6d where a lot of defective walls are observed. Other observation derived from TEM images is that it is of multiwalled type with typical diameter of 54 nm for the CNTs grown from top catalyst coated substrate (Fig. 6b) and 31 nm for CNTs from bottom catalyst coated substrate (Fig. 6a). It is noted from all TEM images that the diameter of CNTs grown from top catalyst coated substrate as in Fig. 6b is much larger than the ones grown from bottom catalyst coated substrate as in Fig. 6a. Currently, no explanation can be provided for the difference in size between the bottom and the top layer nanotubes array.

CONCLUSION

Well-aligned CNTs film, having good array density and diameter distribution, has been successfully grown using all three configurations. This could be a significant finding as it shows the catalyst film may not necessary be exposed directly to the hydrocarbon feedstock in order for nanotubes to grow. The CNTs array also does not exhibit any buckling as a result of the weight of the top substrate, demonstrating the high strength of the CNTs. Having both substrates coated with catalyst will allow for the growth of double layer nanotubes. However, the outcome may not be as clean as single layer nanotubes produced by single catalyst coated substrate. Nanotubes grown from single catalyst coated substrate (Sample 1 and 2) of the sandwich type exhibit equally good quality in terms of density, alignment and purity as the conventional type. Sandwich growth of good quality nanotubes film connecting two substrates will pave the way for the development of application for two terminal devices (Dekker, 1999; Fan *et al*., 2000).

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