Continuous Growth of Vertically Aligned Carbon Nanotubes Forests

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ABSTRACT

Vertically aligned carbon nanotubes (VACNTs), sometimes called forests or carpets, are a promising material due to their unique physical and scale-dependent properties. Continuous production of VACNTs is required for their possible applications in electronic devices, fuel cells and structural materials among others. Chemical vapour deposition (CVD) is the only available technique to produce large areas of VACNTs, however most of the studies that use this technique are performed with stationary growth in batch CVD processing.

In the present work, a desktop continuous growth apparatus has been designed and implemented to grow VACNTs on silicon wafers continuously. We have demonstrated and reported the ability to manufacture VACNT arrays in a continuous manner, significantly reducing the time spent, energy consumed, and reaction products created as compared to batch processing.

Keywords: carbon nanotubes, chemical vapour deposition, manufacturing

1 INTRODUCTION

Vertically aligned carbon nanotubes (VACNTs) have certain advantages over bulk carbon nanotubes (CNT) powders and randomly-oriented CNT mats for applications in electronic devices, fuel cells, biosensors and multifunctional aerospace materials [1]. Although CNTs can be synthesized by a variety of methods, only catalytic thermal chemical vapor deposition (CVD) has been shown to produce large areas of aligned CNTs [2, 3]. However, most of the CVD systems are batch processes where the CNTs are grown on a static substrate placed inside a CVD reactor.

As estimated from our standard batch process, only a small fraction of the time (~10%) is actually utilized to anneal the catalyst and synthesize CNTs. The remainder of the time is spent in heating and cooling the furnace, which wastes time, gas supplies and energy. A continous process to synthesize VACNTs will reduce this consumption of time, gases, and energy.

We have designed and implemented a desktop apparatus to continuously grow VACNTs on silicon wafers. The particular CVD process developed in this work has been performed at ambient pressure employing a mixture of ethylene (C_2H_4) and hydrogen (H_2) without introducing oxidizing agents.

In this system VACNTs films can be grown 26 times faster than in our standard batch process, which makes this system attractive from an industrial and environmental perspective.

2 EXPERIMENTAL

A custom cold-wall chamber has been designed to grow the CNTs. In the chamber, a continously moving conveyor belt made of two stainless steel wires has been used to move a silicon growth substrate coated with a, Fe/Al_2O_3 film, a typical CNT growth catalyst used in CVD of CNTs (see Figure 1). The heat was applied by a dual platform resistive heater made of highly doped silicon wafers [1,4].

The 1cm² Si wafer pieces were placed in series on top of the steel wires, just before passing through the dual platform resistive heater. The particular CVD process used in this work has been performed at ambient pressure employing a mixture of ethylene (C_2H_4) , hydrogen (H_2) , and helium (He).

A quartz tube furnace placed inline with the cold-wall reactor was used as a 'pre-heater' to cause thermal decomposition of the gas mixture prior to reaching the growth substrate [4]. The reactant gases are introduced over the substrate through a directed nozzle to attain high-yield CNT growth. By passing the silicon wafer through the dual platform resistive heater, we achieved continous VACNT growth.

The continous growth process was divided in two phases. First the susbtrate was pretreated under H_2/H_2 to condition the catalyst, and then CNTs were synthesized under a reactant mixture of $C_2H_4/H_2/H_2$. The silicon wafers were moved continously up to 1.27 mm/s. Details of the growth process can be found elsewhere [1].

VACNTs' morphology was characterized by measuring array height and by scanning electron microscopy (SEM) inspection of CNT arrays' characteristics. The quality of the carbon nanotubes produced was assessed by Raman spectroscopy and transmission electron microscopy (TEM).

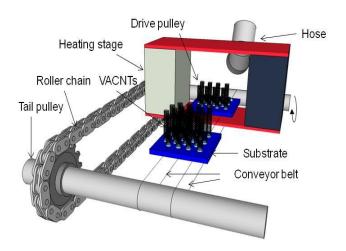


Figure 1: Schematic of the continuous VACNTs production system. The conveyor belt made of two stainless steel wires, was moved by the drive and tail pulley to pass the substrate through the heating stage [4].

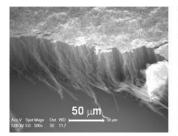
3 RESULTS AND DISCUSSION

Aligned multi-wall carbon nanotube (MWNT) arrays (or "forests") of $60\mu m$ high were obtained, moving the substrate at a speed of up to 1.27 mm/s. The typical wavy and entangled CNT morphology was observed by SEM (see Figure 2). No significant differences were noted between batch-produced CNTs and moving growth CNTs as characterized by SEM and Raman spectroscopy [1]. The CNTs were multi-walled CNTs (MWCNTs) with an average ouside diameter of 15 nm and 10-12 walls. CNT arrays produced on moving substrates were also found to be comparable to those produced through well-characterized batch processes consistent with a base-growth mechanism.

4 CONCLUSIONS

We have demonstrated and reported the ability to manufacture high-yield VACNT arrays in a continuous fashion, thus significantly reducing time, energy consumption, and reaction products relative to batch processing. These characteritics make the system easily scalable to larger production of VACNTs forests.

Future work will include other substrates such as fibers, to create "fuzzy fiber" hybrid advanced composites, and flexible substrates such as stainless steel, which uses the substrate as a catalyst. This system has the potentical to be used in other CVD processes, such as the synthesis of graphene.



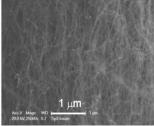


Figure 2: VACNTs grown continuously on a silicon wafer. Detail of a VACNT forest grown on a silicon wafer moved at 1.27cm/min (left) and close-up of the sidewall of the VACNT forest (right)

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REFERENCES

- [1] Figueredo, S.L., Guzman deVilloria, R., Hart, A.J., Steiner III, S.A., Slocum, A.H., and B.L. Wardle, "Apparatus for Continuous Growth of Vertically Aligned Carbon Nanotubes," 9th International Conf. of the European Society for Precision Engineering and Nanotechnology (EUSPEN), San Sebastian, Spain, June 2-5, 2009.
- [2] Terranova, M. L.; Sessa, V.; Rossi, M. The world of carbon nanotubes: An overview of CVD growth methodologies. Chemical Vapor Deposition 2006, 12, 315-325.
- [3] Yasuda, S.; Futaba, D. N.; Yamada, T.; Satou, J.; Shibuya, A.; Takai, H.; Arakawa, K.; Yumura, M.; Hata, K. Improved and Large Area Single-Walled Carbon Nanotube Forest Growth by Controlling the Gas Flow Direction. ACS Nano 2009, 3, 4164-4170
- [4] R. Guzmán de Villoria, S. L. Figuerdo, A.J. Hart, S.A. Steiner III, A. Slocum and B.L. Wardle, "High-yield growth of vertically aligned carbon nanotubes on a continuously moving substrate," Nanotechnology 20, no. 40 (2009): 405611 (8pp).