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Forming carbon nanotube composites by directly coating forests with inorganic materials using low pressure chemical vapor deposition

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ABSTRACT

Low pressure chemical vapor deposition has been used to fill carbon nanotube (CNT) forests with inorganic materials (polysilicon and silicon nitride). Forest filling proceeds by deposition around individual CNTs. As the coating thickness around each CNT increases, the free volume between adjacent nanotubes is filled and finally results in a contiguous composite film. The process maintains the forest height and alignment; however, the coating thickness around the CNTs is in general smaller at the base of the forest than it is at the top. This can cause a contiguous solid film to form at the top of the forest while the forest is only partially filled at the base. Once the top of the forest becomes filled, it prevents growth from occurring at the base. Consequently, the growth process can cap the top of the forest and leave voids between thinly coated CNTs at the base. Such composites have reduced hardness (4 GPa or less). Depositing at reduced temperatures and/or decreased precursor gas flow rates reduces the void fraction through improving the step coverage modulus. This allows one to produce thick (>50 μm) polysilicon-CNT composite films having hardness approximately equal to that of polysilicon thin films (12.4 GPa).

1. Introduction

Carbon nanotubes (CNTs) have captured the attention of the scientific community since their discovery [1]. While graphite is composed of stacks of graphene, CNTs are essentially formed by rolling these graphene sheets [1]. The tubes thus formed are a few nanometers in diameter and as much as millimeters in length. CNTs have been shown to possess an exceptional combination of properties like high electrical conductivity [2], thermal conductivity [3] and mechanical strength [4–6]. This versatility is widely expected to make them valuable for multiple applications — structural composites of various types [5,6], strong textiles [7], transistors [2], interconnects [2], optical limiting [8], biological [9], display [10], charge storage (memory) [11] and an elevator to space [12]. Carbon nanotubes can be produced in clusters as soot-like powder using laser ablation [13], but are often grown as a “forest” or “carpet” of closely packed CNTs on a substrate using processes like chemical vapor deposition (CVD) and Plasma Enhanced CVD (PECVD) [14]. The nanotubes in such a forest can be individually very strong, but the connection between the CNTs and the substrate as well as the interconnection between adjacent tubes is often very weak or virtually non-existent. This allows for easy harvesting of CNTs. Some authors have demonstrated this harvesting by spin-coating a polymer over the forest and peeling it up [15]. Others have pulled CNT threads and sheets directly from forests [7,16]. On the other hand, such a weak connection to the substrate can necessitate delicate handling to avoid serious degradation to the CNT forest. As a consequence, completely filling CNT forests with solidifying materials could have a positive impact on their uses.

CNT-based composites have been a subject of active research for over 8 years [5,6]. Presently, most composites are constructed by dispersing the nanotubes in a matrix of some form. But such processes have inherent difficulties. Challenges include: non-uniform dispersion of nanotubes into the composite (they tend to agglomerate into bundles and ropes) and a lack of adhesion between the CNTs and matrix [5,6]. Thus; the mechanical properties have often been below their theoretically predicted potential. However, filling CNT forests by coating the individual CNTs using a CVD process could bring about advantages. The arrangement of nanotubes in a forest would certainly overcome the issue of CNT non-uniformity in the composite. The level of intertwining of CNTs in the forest could reduce the importance of adhesion through mechanical interlocking. As a result, mechanically stronger structures, electrically more conductive structures and thermally more conductive films can be envisioned.

Before using low pressure chemical vapor deposition (LPCVD), we tried various processes and materials to form fillers. We performed sputtering, evaporation and electroplating of metals as well as PECVD

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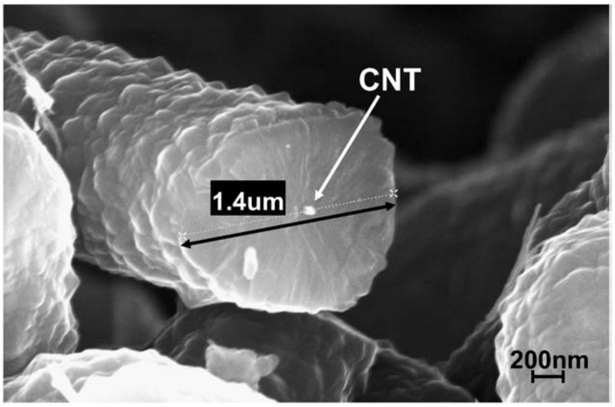

Fig. 1. SEM micrograph of polysilicon coating around an isolated nanotube above a forest. The LPCVD conditions were 630 °C, 33 Pa, 75 sccm silane flow for 40 min.

of fluoro-polymers and diamond like carbon. Unfortunately, none of these methods filled our forests from bottom to top. The deposited material did not penetrate to the bottom of the forest, but instead stuck to the forest top and eventually capped it with a continuous film. This capping phenomenon is caused by the high aspect ratio of the CNTs and their intertwined alignment in our forests. Also, deposition precursors (in a typical physical vapor deposition process) that have a large surface reaction probability will statistically collide with and consequently “stick” to CNTs near the top of the forest. We also tried spin-coating photoresists, spin-on-glass and epoxy into the forests. The spin-coating of liquids tends to mat down the forest, greatly reducing the forest height and CNT alignment.

In this article, we describe the filling of CNT forests with polysilicon (poly-Si) and silicon nitride (Si_3N_4) using an LPCVD process. This is done by coating around the walls of the nanotubes and eventually results in a filled forest. While other authors have used various forms of CVD to coat individual CNTs [17,18] widely spaced CNTs [19,20], or even ropes of CNTs [21] this paper reports the use of LPCVD to form composites by filling dense CNT forests. The main challenge in this is to coat non-uniformly spaced CNT elements in such a way as to form a uniformly and completely filled material. The composites thus formed have been initially characterized by the coating uniformity as well as by their hardness (using a Vickers hardness tester) and sheet resistance. Improved filling of CNT forests using poly-Si is obtained at lower deposition temperatures and lower silane flow rates as predicted by Raupp and Cale's model for the step coverage modulus [22,23].

2. Experiment

An atmospheric-pressure plasma-jet (Surfx Technologies — AtomFlo250D) was used to synthesize CNTs, using helium as the plasma gas and acetylene as the precursor gas injected downstream of the plasma. The substrate was placed on a copper hot plate heated to greater than 600 °C and sitting approximately 1 cm below the plasma-jet source. Substrate temperature calibration was performed using a wafer thermocouple. The substrate was a silicon wafer with a 0.1 µm thick thermally grown oxide layer. 10 nm of catalyst (iron from Alfa Aesar) was evaporated onto the substrate (e-beam evaporation) followed by annealing at 500 °C and in a 0.9×10^5 Pa N_2 ambient for 5 min. In some cases, the iron catalyst was patterned using S1813 photoresist. In such cases, the annealing step was preceded by a lift-off using acetone to remove both the photoresist and undesired iron. The plasma power, substrate temperature and process time could all be varied in order to obtain CNT forests of required quality and height.

A (Tystar) LPCVD stack furnace was used to deposit either poly-Si or nitride (Si_3N_4) into the as-grown CNT forests. The standard deposition conditions for poly-Si (630 °C, 33 Pa, 75 sccm silane) and nitride (730 °C, 33 Pa, 25 sccm CCl_2H_2 and 75 sccm NH_3) result in deposition rates of 15 and 1.7 nm/min respectively. As a consequence, we are able to consistently obtain a 600 nm poly-Si film on a silicon substrate in 40 min and a 400 nm stoichiometric Si_3N_4 film in 240 min.

Scanning Electron Microscopy (SEM) images of the film cross sections were obtained using a (Zeiss-LEO 1530) SEM. We were able to obtain a limited number of hardness measurements at a local company having a Wilson Tukon Machine model LR. The microhardness was measured following an ASTM procedure [24]. Sheet resistances were obtained using an Alessi Four Point probe and a Keithley 2400 source-measure unit. The X-ray diffraction measurements were obtained using a Rigaku Ultima III thin film diffractometer. The copper Kα radiation (0.154 nm) was incident at an angle of 5° from the plane of the substrate.

3. Results and discussion

LPCVD of both poly-Si and nitride proceed by growth around individual CNTs as well as growth from the substrate. Fig. 1 is an SEM micrograph of a poly-Si coated CNT that was isolated from other CNTs at the top of a forest. It shows how the poly-Si growth coats individual CNTs in the forest in a circumferentially uniform fashion. The CNT diameter in our forests varied, but the diameters were always much less than 50 nm. Transmission electron microscopy results indicated that the CNTs were multi-wall having between 5 and 25 walls. We note that the radial thickness of the Si deposit surrounding the CNT is almost the same as that on a bare section of the substrate. This indicates that the growth rates on a planar surface and going radially outward from the CNT are nearly equal, which is not surprising.

In order to obtain this SEM, it was necessary to crack the substrate and pull apart the two pieces. The cracking procedure produced the end to the poly-Si coated CNT seen. We note that the CNT does not extend out of the poly-Si coating nor has it left behind a hole. The CNT and poly-Si appear instead to end at the same plane so that the failure mechanism in this case was not a “sword in sheath” or adhesion issue [5] but rather was a cracking of the CNT itself. Breaks having the CNT extending out of the polysilicon coating did occur but are not seen in that SEM. Since our CNTs were multi-wall and had defects, this is not unexpected; but it also points out a significant advantage to the LPCVD process. The film grows as part of a thermally induced chemical reaction sequence that initially takes place on the surface of the CNT [25,26]. This reaction sequence occurs by the adsorption of SiH_4 to the CNT surface and subsequent pyrolysis to chemisorbed Si. As a consequence, the film adheres to the surface of the CNT. Since the growth conditions are much below the temperature at which Si and C inter-diffuse to any substantial degree [25,26], the result is a poly-Si

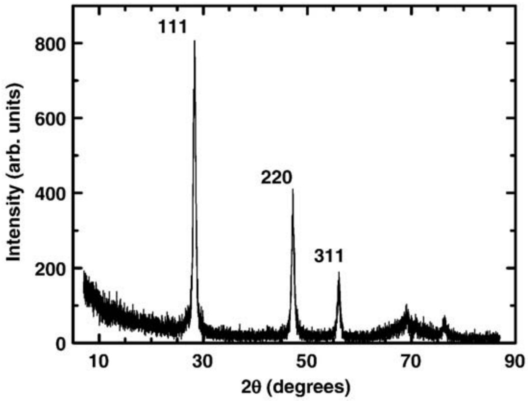

Fig. 2. X-ray diffraction pattern of a CNT–poly-Si composite created using the same conditions as in Fig. 1.