Palladium catalyzed formation of carbon nanofibers by plasma enhanced chemical vapor deposition

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Abstract

A dc plasma enhanced chemical vapor deposition process is used to obtain vertically aligned carbon nanofibers (CNFs) from palladium catalysts using an ammonia–acetylene process gas mixture. Transmission electron microscopy is used to elucidate the microstructure of the as-grown fibers revealing different growth anomalies such as a new secondary growth phenomenon which we term hybrid tip growth. Also included in our analysis are conventional tip growth derived structures. In a few instances, the conventional tip growth derived structures possess elongated catalyst particles that impart small cone angles to the carbon nanofiber microstructure. Detailed microchemical analysis reveals that hybrid tip grown CNFs using thick Pd films are partially filled with Pd. Analysis of these growth phenomenon and implications for potential use as on-chip interconnects are discussed.
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1. Introduction

Vertically aligned carbon nanofibers (CNFs) are readily obtained using plasma enhanced chemical vapor deposition (PECVD) [1]. The physical and chemical characteristics of these structures, in comparison to ideal multiwalled carbon nanotubes, offer inherent processing advantages imparted by their vertical architecture. The vertical geometry is particularly useful in technologies such as nanoelectronics [2], electrodes for biosensing/stimulation [3], nanomechanical [4], and thermal interface materials [5,6]. Many of these technologies require that the interfacial characteristics between the carbon nanofiber and the substrate be tailored for optimal mechanical and/or electrical performance. The critical parameters influencing the CNF interfacial characteristics and microstructure include the choice of catalyst materials and the growth substrate [7]. Typical catalyst materials such as Fe, Co, and Ni have been widely used in PECVD of carbon nanotubes [8]. Other known catalyst metals such as Pd have also been studied [9–11]. Of particular relevance to carbon-based nanoelectronics, palladium has been shown to be particularly useful for achieving reliable ohmic contacts to single walled carbon nanotubes [12]. Contact resistance is currently a critical bottleneck for realizing the full potential of carbon nanostructures in electronics applications.

Carbon nanotubes and nanofibers have been discussed as possible candidates to replace current technologies for on-chip interconnects [13–16]. Bulk transport properties for such interconnect structures [14] need to be related to the physical structure of carbon-based nanostructures. The detailed microchemical and microstructural analysis presented in this letter allows us to examine both the growth mechanism and structure of vertically aligned CNFs to deduce an understanding of possible mechanisms for electron transport in the vertically aligned architecture.

Near ballistic transport has been observed in the Pd–CNT contact configuration [12], proving the worthiness of palladium as a contact electrode for carbon nanostructures. Combining this knowledge with our optimized growth process of PECVD CNFs using palladium as both the catalyst and contact electrode material, we aim to develop a device architecture suitable for use in on-chip interconnect integration schemes.

2. Experimental

2.1. Plasma enhanced chemical vapor deposition

Palladium films (200–2000 Å) were deposited on silicon <100> substrates (pre-coated with a 200 Å titanium barrier layer and 300 Å of nickel) using electron beam evaporation or ion beam sputtering. PECVD of the vertically aligned CNFs was accomplished using a conventional parallel plate dc biased reaction chamber, as described previously [1]. The growth could be assisted using either hot-filament heating and/or using an embedded ceramic heater in the cathode. The plasma discharge was ignited in 4:1 NH_3/C_2H_2 process gas mixture (total flow 100 sccm) at 4 torr. A bias of 500–550 V gives plasma powers between 250 and 400 W and corresponding current densities of 4–6 mA/cm^2 (the cathode area is 98 cm^2). Higher growth rates resulted when higher current densities were employed due to increased substrate heating from the plasma discharge. Upon terminating the glow discharge, C_2H_2 gas was immediately turned off, and the chamber was allowed to cool in flowing NH_3 (80 sccm, 3 torr) for 10–20 min, and then evacuated to 30 mtorr base pressure prior to backfilling with Ar. The samples were then examined using electron microscopy to reveal the morphology and characteristics of the CNFs.

2.2. Electron microscopy and microchemical analysis

A field-emission gun (FEG) scanning electron microscope (FEI DB235) was used to inspect the as-grown Pd-catalyzed CNFs. For transmission electron microscopy (TEM) analysis, CNFs were removed from the substrate, suspended in ethanol, ultrasonicated to separate the nanofibers, and dispersed onto a copper, holey-carbon coated TEM grid. Microstructural and chemical analyses were performed using a FEG TEM (Phillips CM-200). The FEG configuration is required to drive a large current through the sample using a relatively small electron beam size of 14 Å. These conditions provide high spatial resolution, and allow us to selectively perform single particle as well as position dependent chemical composition characterization. The analysis, carried out at room temperature, uses a 200 keV e-beam acceleration energy. Extraneous carbonaceous deposits are minimized due to low levels of contamination in the high-vacuum chamber. Energy dispersive X-ray (EDX) characterization is performed to deduce the chemical composition of particular areas of the CNF. Cross-sectional TEM analysis (JEOL 2000 FX) is also used to directly image the as-grown vertically aligned CNF substrates.

3. Results and discussion

PECVD technologies are critical for high throughput manufacturing, although developing reliable and uniform growth processes for CNFs is still in its infancy. Controlled growth of vertically aligned nanofibers has far reaching implications in the realm of on-chip interconnect design and integration. Three-dimensional integration schemes featuring stacked-device technologies [17] would benefit most from the vertically aligned structures grown using our process. This architecture would allow for shorter global and local interconnect lines, whereby capacitance coupling, inductive effects, and power consumption could be greatly reduced. Local wiring as well as vias for on-chip interconnect structures currently employing fabrication-intensive copper technology could possibly be replaced by vertically aligned nanofibers exhibiting superior thermal, mechanical and electrical properties. Our goal is to study the growth characteristics through variations in process parameters to optimize the microstructural and interfacial characteristics to thus investigate the potential of CNFs and related structures for on-chip interconnect applications.

3.1. Structural characterization by electron microscopy

Vertically aligned CNFs grown from thin palladium layers (<500 Å) exhibited growth characteristics similar to nickel catalyzed growth, albeit at lower density (20% vs. 5%). CNFs nucleated from the thinner palladium layers had diameters between 50 and 150 nm and stacked graphite cone angles of 5–20°. The rationale for using a thin layer of nickel below the palladium layer was to improve contact resistance via nanofiber wetting by the palladium films at the interface or along the nanofiber sidewalls (assuming the Ni layer would indeed be catalytically active). Instead, palladium was able to completely nucleate nanofibers (while no nickel was detected at the tip of the as-grown fibers). Thicker palladium films (2000 Å), however, produced CNFs of varying morphologies across the substrate surface. The normal tip growth morphology was observed, but with a wide variance in stacked graphite cone angles 2–35° (Fig. 1). Fig. 2 shows SEM images of the CNFs obtained from the thick palladium films. Fig. 2a shows the wide variance of CNF diameters obtained (50–200 nm) and we also observed smaller diameter filamentous carbon nanostructures. This initial SEM imaging of the vertically aligned CNFs does not give us much insight into how these smaller carbon nanofilaments are nucleated. Further detailed examination using cross-sectional TEM analysis shows the different types of CNFs obtained across the sample. Fig. 1a shows a low magnification cross sectional TEM image of the palladium catalyzed CNFs. Typically, the CNFs nucleated from thicker films were found to have cone angles between 10 and 20° (Fig. 1b). In rare cases, we also imaged CNFs that possessed cone angles <5° (Fig. 1c). Also in Fig. 1c, the palladium seed is elongated, which dictates the sharp cone angle formation in this particular CNF. It is expected that lowering the cone angle (relative to the fiber axis) will facilitate more efficient charge transfer in the axial direction of the fiber [18], close to that of ideal multiwalled carbon nanotube structure. Indeed, when using either thin or thick films of palladium we obtain a more ideal CNF microstructure at the CNF/palladium interface as described in [19]. Low-temperature electrical modeling further demonstrate the viability of using Pd due to small cone angles resulting in a-axis-like electron conduction through the intrinsic CNF structure [20]. In addition, a small percentage of the CNFs were
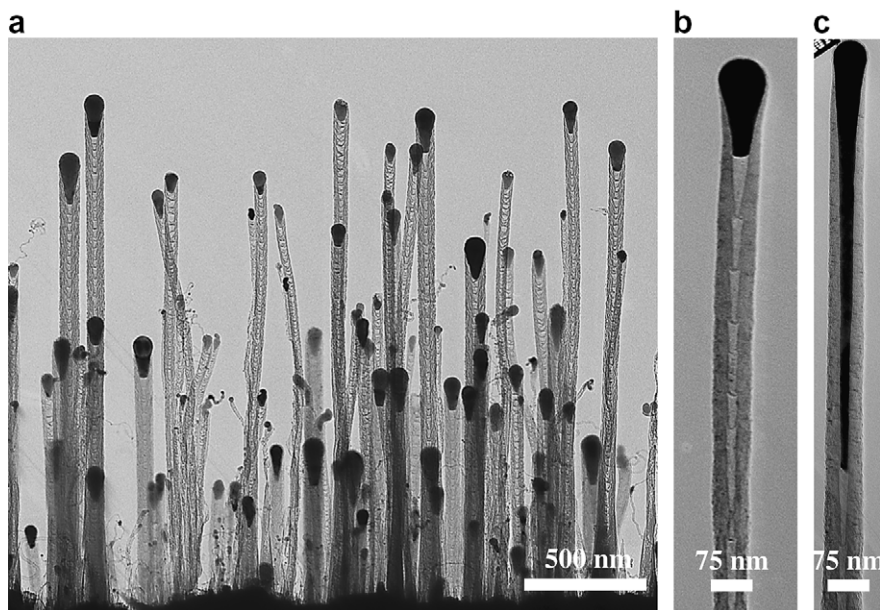
Fig. 1. Low-resolution cross-sectional TEM micrographs showing: (a) carbon nanofiber morphologies observed from thick Pd catalyst; (b) single Pd-catalyzed CNF exhibiting a cone angle of approximately 10–20° and (c) single Pd-catalyzed CNF exhibiting a cone angle of less than 5°. Note the elongated Pd seed particle dictating an extremely sharp cone angle.
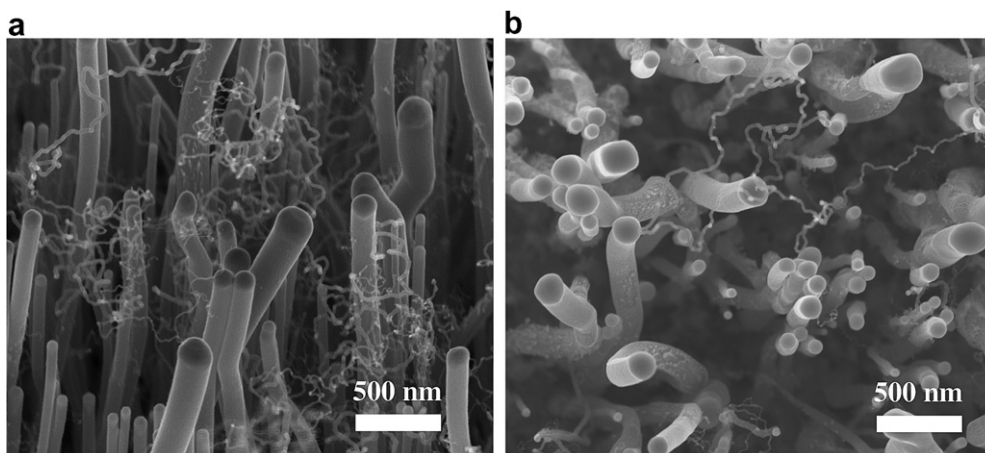

Fig. 2. SEM analysis of Pd derived nanofibers showing secondary/hybrid growth phenomenon. Hybrid tip growth seen from both a 45° view (left panel) and plane view (right panel).

found to have nucleated a smaller secondary carbon nanofiber. We term this phenomenon hybrid tip growth as discussed below.

3.2. High resolution TEM and EDX analysis

The microchemical analysis discussed in Section 2.2 gives rise to observation of novel phenomena in the growth and structure of palladium-catalyzed nanofiber growth. Fig. 3a shows the presence of a palladium nanowire within the CNF as a result of the hybrid tip growth mechanism. A high-resolution view of the region between the main CNF body and the secondary tip growth structure is shown in Fig. 3b. A pinched off portion of the catalyst leads to the

formation and nucleation of the secondary filamentous nanofiber. The presence of palladium filling the inner diameter of the hybrid tip grown nanofiber is confirmed by observing the EDX spectrum shown in the main panel of Fig. 4. The Si signal is residual from the growth substrate while the Cu signal is from the TEM grid. The hybrid tip grown nanofibers observed by TEM are ≈10–20 nm in diameter. The palladium nanowire filling the secondary fiber is ≈15 nm at the site of nucleation, tapering to 5 nm within the inner diameter of the secondary nanofibers over a length of ∼200 nm. These relatively thin dimensions allow us to perform EDX reliably because the probability of inelastic electron scattering events (causing plural peaks in the resulting spectrum) within the sample is unlikely.
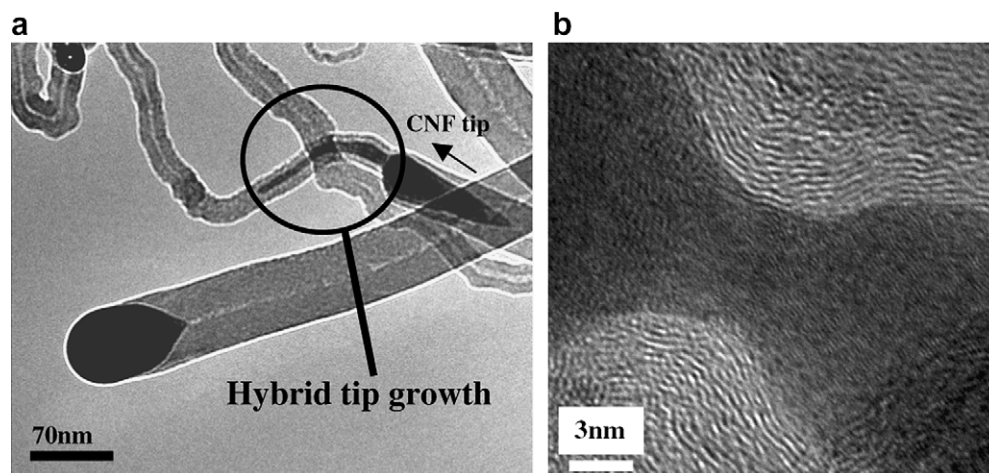
Fig. 3. TEM analysis of secondary Pd growth. Panel (a) shows secondary hybrid tip growth mechanism using conventional TEM. The arrow points towards the tip of the CNF. Panel (b) shows the nucleation site of the secondary nanofiber using high-resolution TEM (HRTEM).
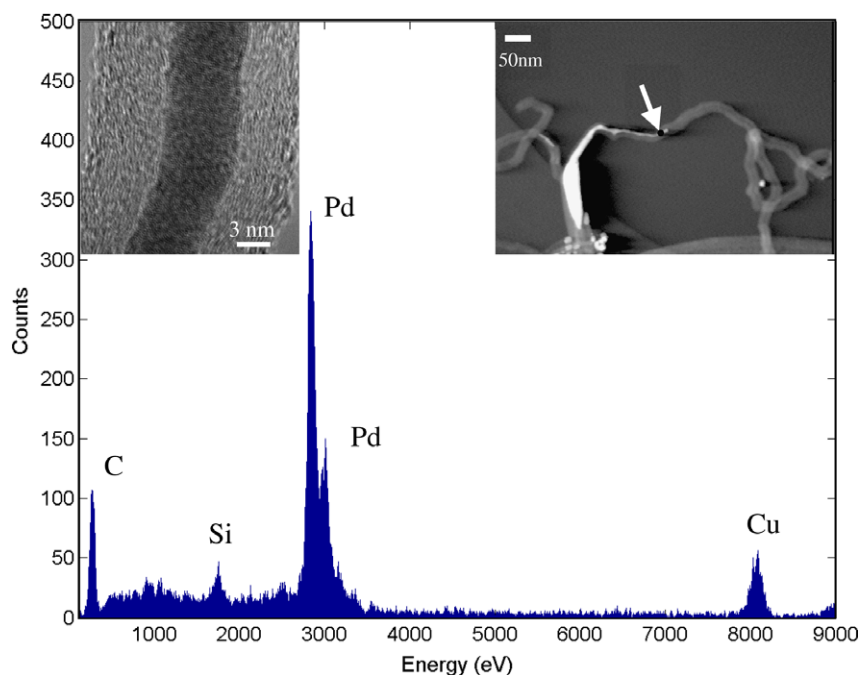

Fig. 4. Energy dispersive X-ray (EDX) for chemical analysis of secondary palladium nanofiber growth. Inset (left): high resolution image of secondary nanofiber filled with Pd. Inset (right): dark-field image of hybrid tip growth. Arrow indicates area analyzed by EDX.

In the carbon filament/whisker growth literature, there are reports discussing the growth of two fibers from a single catalyst particle, termed "bi-directional growth" [21,22]. The growth observed in our work differs from bi-directional growth in that the resulting nanofibers do not exhibit the same dimensions. The hybrid tip-grown CNF has a much smaller diameter than its conventionally grown counterpart. In the case of bi-directional growth, both growth directions result in equal diameter CNFs, and are always symmetrical in shape [22]. Therefore, we believe that this hybrid tip growth can be thought of as a combination of conventional tip growth for the primary CNF and a base growth model for the secondary filament.

4. Conclusion

In this letter, we have described interesting growth anomalies that occur from the Pd-catalyzed formation of vertically aligned CNFs. Two noteworthy observations from high-resolution electron microscopy are presented; thick Pd films lead to a variety of growth morphologies including a hybrid tip growth phenomenon, as well as small cone angles that are imparted by the elongation/wetting of the inner cavity of the CNFs by the Pd catalyst. A remaining challenge is to control these growth phenomena for specific applications. In the case of on-chip interconnect applications, achieving small cone angles has been shown

to reduce the intrinsic resistivity of the CNFs. In addition, palladium could also reduce the contact barrier height for efficient electrical contacting to global wiring schemes in future interconnect architectures. Achieving near-ohmic contact at the nanotube-metal interface as well as investigating the affect of nanotube crystallinity is critical for evaluating and modeling the electrical performance of on-chip interconnects. Continued improvements in the PECVD of carbon nanotubes and related nanostructures is indeed required to explore the potential utility of these structures in advanced applications and future large-scale integration.

Acknowledgments

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