Characterization of Plasma Synthesized Vertical Carbon Nanofibers for Nanoelectronics Applications

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ABSTRACT

We report on the material characterization of carbon nanofibers (CNFs) which are assembled into a three-dimensional (3D) configuration for making new nanoelectromechanical systems (NEMS). High-resolution scanning electron microscopy (SEM) and x-ray electron dispersive spectroscopy (XEDS) are employed to decipher the morphology and chemical compositions of the CNFs at various locations along individual CNFs grown on silicon (Si) and refractory nitride (NbTiN) substrates, respectively. The measured characteristics suggest interesting properties of the CNF bodies and their capping catalyst nanoparticles, and growth mechanisms on the two substrates. Laser irradiation on the CNFs seems to cause thermal oxidation and melting of catalyst nanoparticles. The structural morphology and chemical compositions of the CNFs revealed in this study should aid in the applications of the CNFs to nanoelectronics and NEMS.

INTRODUCTION

Novel logic devices have been actively researched for developing alternative technologies to overcome the severe power consumption and off-state leakage challenges that are now impeding Si transistor scaling. Nanoelectromechanical systems (NEMS) are gaining increasing attention due to their potentials for non-leakage, ultralow-power, and high-speed operations, while at the same time yielding very small footprints [1,2]. Nanotube- and nanowire-based NEMS logic switches have already been demonstrated for a variety of applications [1-5], where the devices are oriented parallel to the substrate (in plane or planar). We consider a scheme where the NEMS switching element is oriented vertically out-of-plane, or perpendicular to the substrate. Ideally this device configuration has a potential to increase integration density by ~10X compared to planar NEMS; and realization of such vertical NEMS switches and arrays may lead to new 3D NEMS logic architectures. Vertically grown carbon nanofibers (CNFs) synthesized by plasma-enhanced chemical vapor deposition (PECVD) offer an interesting device candidate toward this goal, particularly for the many attractive material properties of the CNFs. In this work, we present synthesis and material characterization results of the CNFs using high-resolution scanning electron microscopy (SEM), x-ray electron dispersive spectroscopy (XEDS), and laser irradiation. Such material studies would help lay a solid foundation for engineering CNFs into 3D NEMS for logic switches and other applications.

CARBON NANOFIBER SYNTHESIS AND ASSEMBLY

Aligning nanostructures and arrays with control and precision is highly desired for assembling basic device elements into functional and reliable logic architectures. In the CVD growth of
carbon nanostructures, the electric fields applied during synthesis serves to preferentially orient the nanostructures along the direction of the field [6], which has also been observed in the PECVD synthesis of multi-walled carbon nanotubes (MWCNTs) and CNFs [7,8]. We have also applied the inherent electric fields in plasma growth to develop processes for forming vertically aligned CNFs using dc PECVD, where a gas mixture of acetylene (C2H2) and ammonia (NH3) are used at ~700°C. A stable, uniform dc glow discharge is evident over diameters of ~75mm.

The vertical CNFs in this study are synthesized with pre-patterned nickel (Ni) catalyst nano-islands. Catalyst islands in the 300 nm range are formed adjacent to electrodes using wafer-scale lithographic techniques. After the lift-off process of the electron-beam evaporated catalyst islands, high purity (99.9%) C2H2 and NH3 are introduced at 700°C, which serve as the carbon feedstock and diluent gas, respectively, for the bottom-up chemical synthesis of the CNFs using dc PECVD. The NH3 serves as the etchant gas to remove amorphous carbon deposits, particularly on the catalyst, to facilitate the continued growth of the CNFs. When the desired growth pressure is attained (~5Torr), the dc discharge is ignited at a power of ~200W, and growth is carried out for a fixed duration to realize the desired lengths of the CNFs. Typical CNFs can have lengths of ~1–2µm (or much longer), as illustrations in the SEM image of a fabricated device in Fig. 1.

CARBON NANOFIBER CHARACTERIZATION: RESULTS AND DISCUSSIONS

**High-Resolution SEM and XEDS of Individual Carbon Nanofibers**

Two types of samples have been characterized: CNFs grown on (i) heavily doped single-crystal Si <100> substrate, and (ii) NbTiN/SiO2/Si substrate. High-resolution SEM images in Fig. 2a & 2b (same magnification and scale bar) clearly demonstrate the CNFs and their morphology. Type-(i) CNFs appear to be better aligned vertically, with smooth sidewall morphology, while type-(ii) CNFs are thinner, denser, and less vertically aligned. We have performed high-resolution SEM and XEDS characterization of our CNFs to carefully explore the growth mechanism and quality of the CNFs. These tests are conducted using an FEI Nova 200 dual-beam SEM with Bruker XEDS system. Figure 3a demonstrates a high magnification image of several CNFs from a large forest grown on a Si substrate (type-(i)).

We focus on individual CNFs to explore the materials characteristics and measure XEDS along the length of single CNF at different positions, as highlighted in Fig. 3a. As the measured data in Fig. 3b shows, the Ni concentration is high only at the CNF’s tip, confirming that the Ni catalyst nanodroplet remains at the top during the growth process. At the bottom anchoring point of the CNF no measurable Ni content is detected. In the middle of the CNF, a trace amount of Ni is detected, possibly arising at the surface or sidewalls of the growing CNF. This is likely due to the surface-tension induced formation of ultrasmall Ni droplets which may occur as the main
Ni nanodroplet is being lifted up by the vertically growing CNF during the vapor-liquid-solid process. At the bottom node only C and Si are measurable. A Si peak is detected from the bottom to the top of the CNF, albeit in a decreasing ratio. From high-resolution SEM images such as Fig. 3a, we have also repeatedly observed that the anchoring regions (‘roots’) always have branches, presumably due to the large lattice mismatch between CNFs and the Si substrate.

Figure 2: High-resolution SEM characterization of CNFs. (a) SEM image of vertical CNFs grown on Si <100> substrate; Scale bar is 1µm. (b) SEM image of CNFs grown on NbTiN/SiO2/Si <100> substrate; Scale bar is 1µm.

Figure 3: XEDS characteristics of CNFs grown on Si substrate. (a) High-resolution SEM image of vertical CNFs; Scale bar is 500nm. The three boxes on the CNF (top, middle, bottom) highlight the spots of XEDS measurements. (b) Measured XEDS data from the top, middle and bottom of a single CNF.

Figure 4 shows SEM and XEDS results of CNFs grown on NbTiN/SiO2/Si substrate. The surfaces of these CNFs seem to be less smooth and less uniform (in comparison to CNFs grown on Si), and most of these CNFs are slightly bent and hence less vertical.
Figure 4: XEDS characteristics of CNFs grown on NbTiN/SiO₂/Si substrate. (a) High-resolution SEM image of vertical CNFs; Scale bar is 200nm. The three boxes on the CNF (top, middle, bottom) highlight the spots of XEDS measurements. (b) Measured XEDS data from the top, middle and bottom of a single CNF.

Figure 4b demonstrates measured XEDS from a single CNF, with regions of interest highlighted in Fig. 4a. The top region of the CNF consists of C, Ni, and Ti. Nb and Si clearly decrease from bottom to top along the CNF. In the middle of CNF, one still finds noticeable amount of Ni and Ti, which are not present or measurable in the bottom region of the CNF (see Fig. 4b); and in the middle of CNF an O peak is also observed. During the PECVD growth, both Ni and Ti species elevate with the vertically growing CNF. Small amount of oxidized Ni and Ti clusters or droplets may exist in the middle region of CNF. This may affect the quality and device performance of CNFs. In the bottom region, in comparison to CNFs grown directly on Si, CNFs grown on NbTiN seem to have better anchoring and joint structures with the substrate.

Figure 5: High-resolution SEM characterization of a large array of CNFs subjected to laser irradiation. (a) A large forest of CNFs where a laser beam has been intentionally focused and dwelled for irradiation. (b) A close-in view of the region where the focused laser spot dwelled and passed. (c) & (d) High-magnification zoom-in views (at 25,000× and 50,000× respectively) showing morphology changes of CNFs in laser irradiated region.

Laser Irradiation of Carbon Nanofibers

We have also explored interesting behavior of the CNFs upon irradiation with a laser beam with wavelength \( \lambda = 532 \text{ nm} \). First, irradiation of a forest of CNFs with a laser beam for 0.1 seconds resulted in visual changes of the forest of CNFs that could be observed under an optical
microscope. At relatively high laser irradiation power we have observed morphology and structural changes in the forests of CNFs grown on a Si substrate, as can be seen from the images in Fig. 5; from the SEM image, the tip of the CNF is more susceptible to photon damage.

As shown in Fig. 5d, the originally V-shaped or diamond-shaped Ni catalyst particles on top of some CNFs (i.e., the ones with darker and smoother spherical caps), preferentially result in spherical catalyst regions to reduce surface energy, strongly suggesting melting and resolidification. Similar processes have been widely observed in the final stage of growth of nanoparticles [9]. In some CNFs (see Fig. 5d), the caps are dark and spherically smooth, while in other CNFs the caps are brighter but rougher.

![Image](image.jpg)

**Figure 6**: XEDS characterization of laser irradiation effects on individual CNFs. (a) A high-resolution SEM image (at 100,000×) showing typical CNF structures after laser irradiation, with highlighted spots of XEDS measurements. (b) XEDS data from structures formed at top of CNFs, and (c) typical XEDS data from middle of CNFs.

Our XEDS measurements on individual CNFs help explain these observations. In Fig. 6, it is convincing that the brighter and rougher caps on some of the CNFs consist of oxidized Ni, while the darker ones are Ni spheres that have experienced melting. We note that for photon-induced oxidation, molecular O₂ should be ionized into its smaller atomic components [10]. The ionization energy of O₂ is ~5.1eV and it is exceeding the 532nm photon energy. Therefore, this suggests that the oxidation of the Ni nanocaps is likely a result of a thermally induced process.

**CONCLUSIONS**

We have performed careful material characterization and detailed analysis of individual vertical CNFs grown on both Si and NbTiN/SiO₂/Si substrates, by using high-resolution SEM, XEDS, and laser irradiation. The structural morphology and compositional variations along the body of individual CNFs are analyzed for CNFs grown on both substrates. The observations qualitatively reveal interesting features and technical specifications of the growth mechanism of the CNFs. We expect that the measured material properties and morphology will help the exploitation of these vertical CNFs for developing 3D NEMS and other nanoscale devices.

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