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Morphology engineering of hollow carbon nanotube pillars by oxygen plasma treatment

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ABSTRACT

Oxygen plasma treatment is introduced herein as a novel post-growth fabrication technique to engineer the macroscopic morphology of hollow carbon nanotube (CNT) pillars. Current fabrication techniques for patterned vertically-aligned CNTs only allow for the production of extruded structures with constant cross-sectional area. Oxygen plasma treatment is utilized to rectify this limitation by introducing variation to the cross-sectional area. The results presented herein demonstrate that a conical geometry can be successfully introduced by oxygen plasma treatment to a hollow cylindrical CNT pillar. Using oxygen plasma treatment, the blunt tip of a cylindrical CNT pillar can be controllably sharpened until it reaches a size reduction of more than 93%. A geometric model is presented herein to predict the morphology transformation of a hollow cylindrical CNT pillar during the oxygen plasma treatment. Three distinct phases of CNT structural and morphological evolution induced by oxygen plasma treatment are also identified. A mild CNT functionalization by oxygen adsorbates occurs in the first phase. The second phase is indicated by drastic changes in the macroscopic morphology of CNT pillars. Structural amorphization and collapse of the base of the CNT pillars take place in the final phase.

1. Introduction

Carbon nanotubes (CNTs) represent a multi-functional material with a unique set of structural, electrical, thermal, and fluidic properties that make them attractive for use in numerous applications. However, their widespread use to date has been restricted by a lack of methodology to shape and transport CNTs after their fabrication [1]. Patterned vertically-aligned CNTs, produced by standard nanofabrication techniques of catalyst deposition and chemical vapor deposition, can allow for CNTs to be used in a wide range of applications including stamps for nanoimprint lithography [2], microneedles for transdermal drug delivery [3,4], superhydrophobic surfaces [5,6], electrical and thermal interconnects for microelectronics [1,7,8], field emission sources [9,10], and electrodes for energy storage [11,12]. Nevertheless, current nanofabrication methodology for vertically-aligned CNTs is restricted to extruded geometries with constant cross-sectional area since the pattern of the CNTs is controlled by catalyst patterning on a planar substrate.

In this study, oxygen plasma treatment is introduced as a simple technique to increase the utility of vertically-aligned CNT pillars by enabling true three-dimensional morphology. Specifically, we demonstrate the use of oxygen plasma treatment to engineer the macroscopic morphology of CNT structures by introducing a tapered geometry to hollow cylindrical

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CNT pillars. The ability to introduce a tapered geometry is deemed critical to improve the performance and mechanical stability of CNT pillars in numerous applications, including microneedles, multi-length scale electrical and thermal interconnects, and nanoimprint lithography. Control of the plasma dosage allows oxygen plasma treatments to be used effectively to induce macroscopic shape changes of the CNT pillar in a relatively non-destructive manner. The results presented herein elucidate the effect of oxygen plasma on the evolution of both the macroscopic morphology and the microscopic structure of CNT pillars. Together, the results demonstrate the cascading effect of oxygen plasma treatments from individual nanotubes to large-scale morphology transformations of the CNT pillar.

Oxygen plasma treatments are commonly used as an etching process for cleaning wafers from organic contaminants in top-down fabrication methods. Oxygen plasma treatments are also known as one of the most useful means to introduce oxygen functionalization on graphitic structures, including CNTs and graphene. Numerous previous studies have shown that oxygen plasma produces a large amount of oxygen containing radicals that are readily adsorbed by these materials [13–19]. The adsorption of oxygen alters the highly periodic π-bond networks of graphitic structures, which results in changes in their electrical, mechanical, chemical, and wetting properties. It has also been known that excessive exposure to oxygen plasma treatment often results in irreversible damage to the CNT structure. While oxygen plasma treatment has been used for years to modify the morphology of non-patterned vertically-aligned CNTs [11,18,20], its use to modify the morphology of patterned vertically-aligned CNTs, in particular hollow CNT pillars, is yet to be explored. Because of the relevance of patterned vertically-aligned CNTs, in particular hollow CNT pillars, to numerous applications, as mentioned earlier, it is imperative to elucidate the underlying mechanism governing such modification.

Three distinct phases of CNT structural and morphological evolution induced by oxygen plasma treatment are identified in this study. A mild CNT functionalization by oxygen adsorbates occurs in the first phase. The second phase is indicated by drastic changes in the macroscopic morphology of CNT pillars. Structural amorphization and collapse of the base of CNT pillars take place in the final phase. The morphology evolution of the CNT pillar is approximated by a geometric model that can be used to effectively predict the shape of tapered pillars after oxygen plasma treatment. Altogether, the results presented herein demonstrate the potential of oxygen plasma treatment as a post-growth fabrication technique to engineer the macroscopic morphology of aligned CNT structures.

2. Materials and methods

Pillars of vertically aligned multi-wall carbon nanotubes (CNT) are fabricated by thermal chemical vapor deposition (CVD) method. Aluminum oxide buffer (Kurt J. Lesker, 99.99% purity) and iron catalyst (Kurt J. Lesker, 99.95% purity) layers are patterned on silicon wafers (El-Cat Inc., polished 300 nm thermal oxide) prior to the CNT growth using standard photolithography and e-beam evaporation (CHA Industries, Mk 40 e-beam evaporator) techniques. The thickness of the buffer and catalyst layers is 10 nm and 1 nm respectively. CVD of CNT pillars is performed using a mixture of ethylene (Matheson, 99.95% purity) and hydrogen (Airgas, 99.999% purity) in a 1-inch tube furnace (Lindberg Blue M, Mini Mite). Details of the CVD condition are described elsewhere [21–23]. The height of CNT pillars used in this study is varied between 200 μm and 800 μm. The as-grown CNT pillars used in this study are in the shape of a hollow cylindrical pillar with outer and inner diameters of 50–150 μm and 25–120 μm respectively.

After fabrication, CNT pillars are exposed to oxygen plasma treatment using a remote RF oxygen plasma etcher (PVA Tepla, M4L) at a power setting of 50 W, an oxygen flow rate of 100–150 sccm, and a chamber pressure of 500 mTorr [22]. The as-grown CNT pillars, together with their growth substrates, are placed at the center of the chamber to ensure the uniformity of plasma exposure during the oxidation process. The exposure time is varied between 1 and 20 min.

Changes in macroscopic morphology of CNT pillars are characterized using a field emission scanning electron microscope (Zeiss, 1550 VP). Scanning electron micrographs are taken at a sample tilt angle of 60° using an acceleration voltage of 5 kV. Local oxygen to carbon atomic ratio (O/C) is measured on specific CNT pillars by performing energy dispersive X-ray spectroscopy (EDS) (Oxford, X-Max Silicon Drift Detector) at an acceleration voltage of 5 kV. Changes in the microscopic structure of CNT pillars are characterized using a high performance transmission electron microscope (FEI, Tecnai F30UT). Transmission electron micrographs and selected area diffraction pattern (SADP) are collected with an acceleration voltage of 300 kV. For TEM and SADP, each sample is prepared by scraping off a small amount of CNT pillars from their growth substrates and dispersing the CNTs in ethanol (Sigma Aldrich, 200 proof) under sonication for 5 min. This dispersion is then poured on a holey carbon grid (Electron Microscopy Sciences, C-Flat) and dried in low vacuum at room temperature.

Surface chemistry characteristics of CNT pillars are assessed using X-ray photoelectron spectroscopy (XPS) (Surface Science, M-Probe XPS). A monochromatic 1486.6 eV Al Kα is used as the X-ray source and the detailed C1s spectra are collected at a binding energy of 281–297 eV and a spot size of 100 μm. Each sample is prepared from the dispersion of CNT pillars mentioned above, which is then poured uniformly on a clean silicon chip and dried in low vacuum at room temperature. Changes in relative surface concentration of various C bonds are quantified by performing deconvolution on the C1s spectra using Gaussian–Lorentzian peak fitting with Shirley baseline correction at the following binding energies: C—C sp2: 284.7 ± 0.1 eV (FWHM 0.9 eV), C—C sp3: 285.6 ± 0.1 eV (FWHM 1.3 eV), C—O: 286.6 ± 0.1 eV (FWHM 1.4 eV), C═O: 287.4 ± 0.2 eV (FWHM 1.4 eV), O—C═O: 289 ± 0.4 eV (FWHM 1.7 eV), O—C(O)═O: 290.4 ± 0.4 eV (FWHM 1.7 eV), and π–π^*: 292.1 ± 0.4 eV (FWHM 1.6 eV) [13,17,23].

Raman spectroscopy characterization is performed using a micro Raman spectrometer system (Renishaw, M1000) equipped with an argon ion laser at an excitation wavelength of 514.5 nm. Each sample is characterized as is without prior sample preparation. Raman spectra are collected using an optical magnification of 100× in a non-polarized mode at a Raman shift of 500–3500 cm^{-1}. Three CNT signature peaks

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