Generating Suspended Single-Walled Carbon Nanotubes Across a Large Surface Area via Patterning Self-Assembled Catalyst-Containing Block Copolymer Thin Films

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Using self-assembled block copolymers as templates, catalytically active nanostructures with controlled size and space have been produced. A self-assembled polystyrene-b-polyferrocenylsilane thin film and monolayer of surface micelles of cobalt-complexed polystyrene-b-poly(2-vinylpyridine) are fully compatible with novolac-based conventional photoresists. Combining bottom-up self-assembly of catalyst-containing block copolymers with top-down microfabrication processing, plateaus covered with arrays of catalytically active nanostructures have been generated. Spatially selective growth of suspended single-walled carbon nanotubes over a large surface area has been achieved. Greatly enhanced Raman signals have been detected from the suspended tubes. This facile method of creating highly ordered catalyst nanostructures on top of posts enables the rational synthesis of suspended carbon nanotubes, thus facilitating the study of CNT properties by optical methods and enabling the fabrication of devices based on suspended CNTs.

Carbon nanotubes (CNTs) have become one of the most studied materials due to their exceptional mechanical, electronic, and chemical properties. Over the past several years, a host of possible applications have been validated, bolstered by experimental results. Such applications include composite materials to improve mechanical properties and thermal and electrical conductivities of the bulk products,1 field-emission-based flat panel displays,2 novel semiconducting devices in microelectronics,3,4 chemical and biological sensors,5,6 and most recently nanoelectromechanical systems (NEMS), suspended carbon nanotubes across trenches with ends in contact with electrodes are required. Several new device concepts have been developed and demonstrated in the past several years that utilize free-standing tubes. For example, it has been reported that bending and stretching of a suspended nanotube can induce significant changes in resistance. Therefore, ultrasmall mechanical sensors or resonators and new types of strain gauges can be generated using suspended CNTs.7 As another example, CNT-based nanoelectromechanical switches that utilize suspended CNTs mechanically deflected to establish electrical contact to a metal have also been demonstrated.8a,8b In addition, nanoelectromechanical oscillators have been demonstrated by suspended tubes for the potential use in ultrasensitive mass detection and radio signal processing.8 Suspended tubes not only offer great technological promise but also are important for fundamental research. Because suspended tubes are free of van der Waals interaction with the underlying substrate, they are preferable for studying CNTs by optical techniques. Raman spectroscopy has been the most effective tool to determine SWNT diameter.10 There have been experimental indications that the strong interaction between CNTs and their support reduces and shifts the Raman signals generated from lattice vibration of the CNTs. Recently an ideal p–n junction diode showing significant power conversion has been produced using a suspended tube.11 The use of a suspended CNT avoids the interaction between the CNT and surface that generates states in the band gap leading to nonideal behavior. Most recently, greatly enhanced infrared emission has been observed from suspended tubes. This result suggests that the interaction with the underlying substrate could be the main source for nonradiative recombination.12 All these findings indicate that suspended tubes are much more desirable for fundamental research of CNT properties, such as diameter and photoconductivity and electroluminescence behaviors.

Over the years, several methods have been used to fabricate suspended CNTs. Casting a solution of pre-synthesized CNTs onto a surface consisting of an array of trenches has been widely used. However, the location and density of suspended CNTs cannot be controlled. Post-growth etching techniques such as wet etch to produce trenches underneath the CNTs may damage and sag the CNTs. More elegant methods have been recently developed such as stamping a mixture of iron and molybdeneum salts with Al2O3 nanopowders on etched Si posts.13 This is a robust system for CNT growth but it provides no means to control the catalyst size and resulting CNT diameter. Since CNT properties are closely related to diameter, it is highly desirable to control diameter of suspended CNTs for enabling fabrication...
and commercialization of suspended CNT-based devices. To improve diameter control of CNTs, block copolymer templates have been proposed to rationally synthesize catalyst nanoclusters on which CNTs grow.\textsuperscript{14-16} Catalyst systems derived from block copolymer templates, such as a self-organized polystyrene-\textit{b}-polyferrocenylethylmethylsilane thin film, highly ordered surface micelle monolayer of cobalt-complexed polystyrene-\textit{b}-poly(2-vinylpyridine), and an iron-exchanged polystyrene-\textit{b}-poly(acrylic acid) surface micellar thin film, have been able to produce uniformly sized and spaced catalyst nanostructures. Especially, both the iron-containing nanostructures derived from polystyrene-\textit{b}-polyferrocenylethylmethylsilane and cobalt nanoparticles synthesized from the polystyrene-\textit{b}-poly(2-vinylpyridine) template have been able to produce very small CNTs with narrow size distribution. Lithographically selective growth of CNTs on a surface using these two catalyst systems has been demonstrated.\textsuperscript{14-16} In this report, using conventional semiconductor image transfer processing, we have created ordered arrays of catalyst nanostructures surmounted on posts. We have grown suspended single-walled carbon nanotubes across trenches at predefined locations over a large surface area using this approach. This is the first report of using uniform catalyst nanostructures derived from block copolymer templates to fabricate lithographically controlled suspended CNTs. The method of producing suspended CNTs described herein is simple, robust, and can be integrated into existing semiconductor processes. It can be easily scaled to wafer-size processing, which is more advantageous than other previously published methods. The ability to manufacture suspended CNTs with controlled location, density, and diameter will allow thorough investigation and characterization of CNTs by various optical means and provide a manufacturing pathway for the fabrication of CNT-based electromechanical and photovoltaic devices as well.

In this study, catalyst-containing nanostructures were synthesized from self-assembled catalyst-containing block copolymers templates where an iron or cobalt catalyst species was incorporated onto one segment of a block copolymer. The iron-containing diblock copolymers were synthesized via sequential living anionic polymerization of styrene and silaferrocenophane to produce polystyrene-\textit{b}-polyferrocenylethylmethylsilane (denoted PS-\textit{b}-PFEMS).\textsuperscript{16} A combination of gel permeation chromatography and \textsuperscript{1}H NMR revealed that the mean number of repeat units of polystyrene was 402 and that of polyferrocenylethylmethylsilane was 98, giving an approximate volume fraction of PFEMS of 0.33. A 0.15 wt % toluene solution was spin-coated on a Si substrate with a 500 nm thick, thermally grown silicon oxide. After solvent annealing, a periodically ordered array of PFEMS domains surrounded by a polystyrene matrix was formed as shown in Figure 1a. UV-ozonation converted the PFEMS cylindrical domains into iron-containing silicon oxide nanostructures. This type of nanostructure was an excellent catalyst system for producing high quality, single-walled CNTs.\textsuperscript{14} The cobalt-containing block copolymer system was prepared by selectively attaching cobalt species onto the poly(2-vinylpyridine) block of a polystyrene-\textit{b}-poly(2-vinylpyridine) (denoted PS-\textit{b}-P2VP). The PS-\textit{b}-P2VP with 475 repeat units of PS and 141 repeat units of P2VP was purchased from Polymer Source. After complexation with cobalt, the cobalt-complexed PS-\textit{b}-P2VP formed spherical micelles in toluene whose cores consist of cobalt-complexed P2VP blocks encapsulated by PS chains.\textsuperscript{15} Depositing the spherical micelles onto a properly treated silicon oxide surface, a monolayer of surface micelles was thus produced as displayed in Figure 1b. UV-ozonation removed all the organic components and converted cobalt-complexed P2VP cores into cobalt oxide nanoparticles. This catalyst system exhibited superb ability to initiate the growth of high quality CNTs with a minimum number of defects.\textsuperscript{15}

Figure 2 is a schematic diagram that depicts the process used to generate suspended CNTs. A catalyst-containing diblock copolymer solution was first spin-coated onto a Si wafer with a 500 nm thick thermally grown silicon oxide film. Upon spin-coating of cobalt-complexed PS-\textit{b}-P2VP, a monolayer of highly ordered cobalt-loaded surface micelles was directly formed. After coating the PS-\textit{b}-PFEMS solution, solvent annealing in toluene was then performed to promote the self-assembly process. Once the highly ordered cobalt- and iron-containing films as shown in Figure 1 were formed, thermal treatment at $120^\circ$C for 20 min was conducted to completely remove solvent for circumventing possible intermixing between a photoresist and a silicon oxide surface. After thermal treatment, the polystyrene matrix was formed as shown in Figure 1a. UV-ozonation converted the PFEMS cylindrical domains into iron-containing silicon oxide nanostructures. This type of nanostructure was an excellent catalyst system for producing high quality, single-walled CNTs.\textsuperscript{14} The cobalt-containing block copolymer system was prepared by selectively attaching cobalt species onto the poly(2-vinylpyridine) block of a polystyrene-\textit{b}-poly(2-vinylpyridine) (denoted PS-\textit{b}-P2VP). The PS-\textit{b}-P2VP with 475 repeat units of PS and 141 repeat units of P2VP was purchased from Polymer Source. After complexation with cobalt, the cobalt-complexed PS-\textit{b}-P2VP formed spherical micelles in toluene whose cores consist of cobalt-complexed P2VP blocks encapsulated by PS chains.\textsuperscript{15} Depositing the spherical micelles onto a properly treated silicon oxide surface, a monolayer of surface micelles was thus produced as displayed in Figure 1b. UV-ozonation removed all the organic components and converted cobalt-complexed P2VP cores into cobalt oxide nanoparticles. This catalyst system exhibited superb ability to initiate the growth of high quality CNTs with a minimum number of defects.\textsuperscript{15}

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A temperature of 120 °C was chosen because it is well above the boiling temperature of toluene but below the order-to-disorder transition temperatures for both catalyst-containing diblock copolymer systems. OCG825, a highly sensitive broadband photoresist, was then applied on top of these two ordered block copolymer films respectively at a spin speed of 3000 rpm for 30 s to afford a 1.2 μm thick film. An ASML 2540 I-line stepper was used to expose the photoresist. A metal ion-free developer, 1:1 water diluted Arch OPD262, removed the exposed resist to generate resist patterns. Further image transfer was accomplished in an Unaxis SLR 770 inductively coupled plasma (ICP) etcher. A mixture of 1 sccm of Cl₂ and 14 sccm of Ar was first introduced to remove the self-assembled catalyst-containing polymer films. After the removal of the polymeric layers, 40 sccm of CF₄ was introduced to etch the SiO₂ underlayer. Finally, 40 sccm of O₂ was used to remove any carbon redeposited on the sidewall. After stripping the photoresist, UV—ozonation converted the catalyst-containing polymer film into either cobalt oxide nanoparticles or iron-containing silica nanostructures on top of the posts (posts and plateaus are used interchangeably). Insets in Figure 2 are AFM height images of metal-containing nanostructures (AFM height images: 0.5 μm by 0.5 μm scan, 10 nm in height). (e) CNT suspended across a trench.


Figure 3 Low magnification SEM image of suspended tubes across a 1 μm wide trench with the depth of 250 nm synthesized using iron-containing nanostructures. The inset is the corresponding high magnification image.

Figure 2. (a) Self-assembled catalyst-containing block copolymer film on SiO₂ (blue color). (b) Patterned photoresist film on top of the catalyst-containing self-assembled polymer film. (c) Resist pattern transferred into the catalyst-containing polymer film and thermally grown silicon oxide by ICP etching. (d) Catalyst-containing nanostructures after solvent strip of photoresist and UV—ozonation removing all the organic components. The insets are AFM height images of metal-containing nanostructures (AFM height images: 0.5 μm by 0.5 μm scan, 10 nm in height). (e) CNT suspended across a trench.

Figure 3. Low magnification SEM image of suspended tubes across a 1 μm wide trench with the depth of 250 nm synthesized using iron-containing nanostructures. The inset is the corresponding high magnification image.

Figure 3 are low and high magnification SEM images of suspended tubes synthesized using iron-containing nanostructures prepared from the self-assembled PS-b-PFEMS thin film. SEM inspection indicated that both catalyst-containing systems were compatible with the conventional novolac-based photoresist process and suspended CNTs at predefined locations over a large surface area were produced. It was also noticed that the density of suspended tubes was reduced from holes to trenches since the surface around a hole is capable of capturing all the tubes grown radially in every direction. The number of suspended tubes decreases significantly with wider or deeper trenches. This phenomenon can be explained as follows. It is acknowledged that whether CNT growth proceeds via the tip
or base growth mechanism, the growth ends are not attached onto a surface but rather are lifted away from the surface. Thus as trenches become wider or deeper the probability of growth ends hopping across the trench decreases.

Raman analysis was used to examine Raman signal intensity of free-standing tubes and tubes attached onto a surface. The set of Raman intensity maps shown in Figure 4a are the silicon peak at 520 cm\(^{-1}\), G-band at 1590 cm\(^{-1}\), and CNT radial breathing mode between 160 cm\(^{-1}\) to 230 cm\(^{-1}\), which were collected from the CNT sample using cobalt catalyst. The white lines correspond to the edges of a trench with a 0.5 \(\mu\)m depth and a 5 \(\mu\)m width. The silicon signal in the trench region as expected is lower than on the posts. The intensity of G band suggests that there are several CNTs on the posts and at least one tube across the trench. The Raman shift indicates that the diameter of the suspended tube is 1.2 nm and a possible \((n,m)\) assignment is (13,4). Raman signal intensity comparison of the two corresponding regions indicates that the greatly enhanced

Figure 4. (a) Raman analysis of CNTs synthesized from cobalt nanoparticles. (i) Raman intensity map of a 10 \(\mu\)m by 10 \(\mu\)m region around a trench. (ii) Raman spectra of CNT produced from cobalt catalyst nanoparticles, suspended tubes over the trench in blue and tubes attached on surface in red. The inset is the SEM image of suspended CNTs produced from the cobalt catalyst. (b) Raman spectra of CNTs produced from iron-containing nanostructures.
Raman signal is produced from free-standing CNTs. This suggests that the suspended tubes are free of van der Waals interaction with the substrate. For CNTs attached on the post, the interaction of CNTs with the underlying surface may impede the radially mechanical oscillation of CNTs, thus yielding weaker Raman signals. Figure 4b is another side-by-side comparison of Raman spectra of CNTs produced from iron-containing nanostructures. This result further confirms that the absence of substrate interaction results in a greatly enhanced Raman signal. Therefore, they are desirable for accurate determination of tube diameters.

In conclusion, self-assembled catalyst-containing block copolymer films are capable of producing highly ordered catalyst-containing nanostructures with uniform size. The aforementioned self-organized catalyst-containing block copolymer films are compatible with novolac-based photoresists and thus can be patterned using conventional semiconductor processing. Posts surmounted with periodic and uniform-sized catalyst-containing nanostructures have been created by photolithography and subsequent etch. We have demonstrated that this block copolymer template approach is capable of producing suspended CNTs at predefined locations. The enhanced Raman signals generated by suspended CNTs are useful for accurate determination of CNT diameters by Raman spectroscopy. This method for producing suspended tubes is expected to facilitate the characterization of CNTs by optical means and harness suspended tubes for device applications.

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References and Notes