Integration of suspended carbon nanotube arrays into electronic devices and electromechanical systems

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A synthetic strategy is devised for reliable integration of long suspended single-walled carbon nanotubes into electrically addressable devices. The method involves patterned growth of nanotubes to bridge predefined molybdenum electrodes, and is versatile in yielding various microstructures comprised of suspended nanotubes that are electrically wired up. The approach affords single-walled nanotube devices without any postgrowth processing, and will find applications in scalable nanotube transistors (mobility up to 10 000 $cm^2/V\,s$) and nanoelectromechanical systems based on nanowires. [DOI: 10.1063/1.1497710]

It is desired to electrically contact suspended single-walled carbon nanotubes (SWNTs) for various fundamental studies and potentially applications. The fact that a suspended nanotube is free of van der Waals interactions with a substrate makes them appealing for mechanical, electrical, and electromechanical measurements. For instance, Tombler *et al.* have used suspended SWNTs to investigate how reversible structural deformation in nanotubes affects their electrical properties.[1] Several postgrowth fabrication methods have been developed for making electrical contact to suspended nanotubes.[1–5] One approach involves the growth of a nanotube across a trench, followed by microfabrication processing steps to form electrode pads at the two sides of the suspended tube.[1] A second approach involves chemical etching of the substrate on which a nanotube is resting.[2–4] These approaches are limited to short ($<0.5\ \mu$m) suspended nanotubes since wet processing in solvents and resist solutions tend to "rip" suspended nanotubes, due to forces related to viscous fluidic flow or surface tension.

Suspended SWNTs 5 to 100 μm have long been synthesized previously by patterned chemical vapor deposition (CVD) growth on substrates with elevated structures.[6,7] In earlier attempts to form electrical contacts to these nanotubes using the aforementioned methods, we observe that suspended nanotubes sag or are swept away after wet processing steps during microfabrication.

Here, we describe an approach to wire up SWNTs electrically in a noninvasive manner. The method is general to suspended nanotubes with arbitrary lengths, but can also be applied to nanotubes supported on flat substrates. We find that a refractory metal, molybdenum (Mo) is compatible with high-temperature SWNT synthesis. Arrays of Mo electrode pairs are first fabricated on a substrate, SWNTs are then grown from electrodes to opposing electrodes to form bridges that electrically connect the electrodes. We show that this approach affords electrical circuits of SWNTs suspended over various microstructures. The suspended nanotubes thus grown can be measured electrically right after growth.

Figure 1 shows the process and results for growth of SWNTs suspended between Mo electrodes on top of two elevated SiO_2 terraces. The starting substrate is a p-type silicon wafer with 2 μm thermally grown oxide. A 50 nm thick Mo film is first deposited on the wafer by sputtering [Fig. 1(a)]. Subsequently, photolithography and dry etching (reactive ion etching in SF_6 and C_2ClF_5 for removing Mo not protected by a photoresist) are used to form two opposing Mo electrodes on SiO_2, followed by the use of 6:1 buffered HF to etch down the SiO_2 around the Mo electrodes by 1.5 μm. The photoresist on top of the Mo pattern is then removed for the catalyst-patterning step. The substrate is coated with 1.6 μm thick of poly(methylmethacrylate) (PMMA), patterned with deep ultraviolet light or electron beam, and developed to form wells in the PMMA film. An alumina-supported iron catalyst suspended in methanol is then spun onto the substrate followed by lifted off in acetone.[8,9] This leads to two catalyst islands formed on the two opposing Mo electrodes on top of the SiO_2 terraces [Fig. 1(b)]. Other fabrication schemes for such substrate preparation have also been successful. For instance, one can first pattern catalyst on the Mo film, followed by defining the Mo electrodes, and the subsequent formation of Mo/SiO_2 terraces by wet etching.

Growth of SWNTs from the patterned catalyst islands is carried out in a 1 in. CVD system. The growth takes place under a 72 mL/min flow of methane (99.999%) and a 10 mL/min co-flow of hydrogen at 900 °C for 5 min.[10] During heating and cooling of the CVD reactor, a constant flow of pure H_2 is used to eliminate the possibility of oxygen impurities in the gas oxidizing the Mo electrodes.

Using molybdenum as an electrode material is key to this work. Mo is the only metal found to be compatible with our CVD growth of SWNTs at high temperatures. Other metals, including gold (Au), titanium (Ti), tantalum (Ta), and tungsten (W) have all failed for various reasons. After CVD growth, Au electrodes become discontinuous as gold balls up due to its relatively low melting temperature. Ti and Ta electrodes also fail as they become partially etched and thus highly resistive after growth. The etching phenomenon is explained by the formation of volatile metal hydrides at high temperatures in an environment containing hydrogen.[11] This

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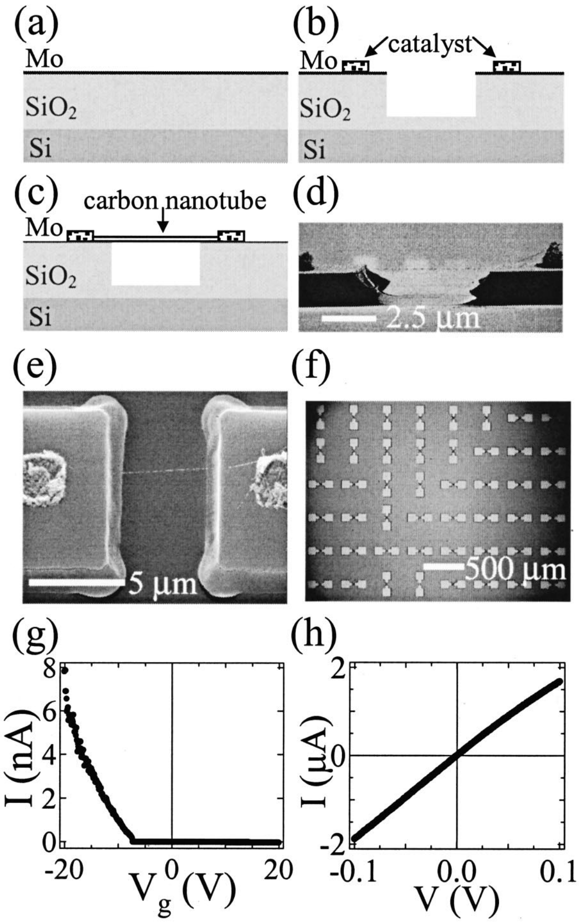

FIG. 1. Synthesis for electrically connected suspended SWNT devices. (a) a 50 nm thick Mo film is sputtered on a SiO_2/Si wafer. (b) formation of Mo/SiO_2 terraces with patterned catalyst islands on top of the Mo electrodes. (c) growth of a SWNT from electrode to electrode, forming a suspended nanotube bridge across the Mo/SiO_2 terraces. (d) SEM side view of a device. (e) SEM top view of a device. Samples for SEM are coated with 20 nm of Au in order to visualize the tube suspension clearly. (f) optical image of an array of devices. (g) $I-V_g$ curve for a suspended nanotube FET. Bias voltage = 10 mV. (h) I–V curve for a 50 kΩ metallic suspended SWNT.

chemical incompatibility eliminates hydride-forming metals as electrode materials for nanotube growth at elevated temperatures. Mo and W are among the metals that do not form hydrides and are stable against aggregation at high temperatures. However, although W electrodes do survive the CVD growth process with high connectivity and conductivity, no SWNTs are found to grow from catalyst patterns on the W electrodes. The presence of W near the catalyst material appears to inhibit the growth of nanotubes, presumably caused by the high catalytic activity of W towards hydrocarbons,[12] which interferes with SWNT formation in the CVD process.

With Mo electrodes, SWNTs are frequently found to grow from electrodes to opposing ones, resulting in devices comprised of suspended nanotubes bridging pairs of Mo electrodes [Fig. 1(c)]. We find that the Mo electrodes exhibit excellent conductivity after growth and allow for ohmic contacts with nanotubes. This leads to suspended SWNT devices that can be measured electrically without any processing after nanotube synthesis. Figures 1(d) and 1(e) show representative scanning electron microscopy (SEM) data of individual SWNTs bridging two Mo electrodes on top of SiO_2

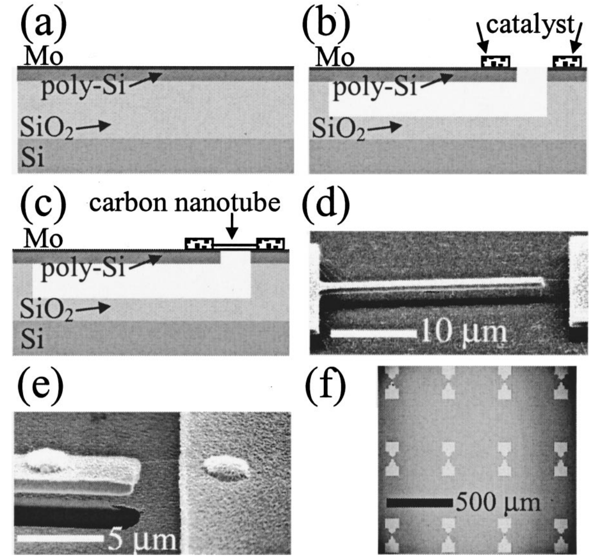

FIG. 2. Growth of electrically addressable suspended SWNTs integrated into Si micromechanical structures. (a)–(c) schematic process flow. (d) and (e) SEM images of a device. (f) Optical images of an array of devices.

terraces. The SEM images show that the nanotubes originate from catalyst islands and span the trench between the two electrodes. The lengths of the suspended portion of the SWNTs are 3–10 μm, but can be either much shorter or longer. The portions of the nanotube overlapping with the Mo electrode surfaces provide electrical contact to the nanotube.

Figures 1(g) and 1(h) show representative electrical properties of individual as-grown SWNTs suspended over Mo/SiO_2 terraces. The field-effect transistor (FET) like current (I) versus gate-voltage (V_g) characteristics in Fig. 1(g) corresponds to a p-type semiconducting SWNT due to oxygen doping.[13,14] The gate voltage is applied to the Si substrate, 2 μm away from the nanotube separated by an air gap and 0.5 μm thick oxide. Nevertheless, the Si backgate is still sufficient to increase or deplete carriers in suspended tubes. The ON state resistance of our suspended semiconducting SWNTs is typically $\sim 100\ k\Omega - 1\ M\Omega$, comparable to those grown on flat SiO_2 substrates and electrically contacted postgrowth.[15] We have also observed a fraction of the suspended SWNTs with much weaker gate dependence, which corresponds to metallic or quasimetallic SWNTs. The resistance of these tubes can be tens of kilo-ohms (lowest resistance $\sim 20\ k\Omega$ thus far) with linear current versus voltage $I-V$ curves [Fig. 1(h)]. These results demonstrate that our fabrication and growth approach leads to highly ohmic contacts to suspended SWNTs. However, the precise nature of the nanotube-Mo contacts remains to be determined. We speculate that metallic carbide bonding at the interface is possible due to the elevated growth temperature.

The idea of growing nanotubes between metal electrodes compatible with CVD is powerful in yielding various suspended SWNT devices that are impossible or difficult to obtain by any other postgrowth fabrication methods. In Fig. 2, we show a second example of suspended SWNT device that not only can be addressed electrically, but also mechanically and electromechanically. The individual SWNT bridges a micromechanical poly-Si cantilever and a terrace [Fig. 2(d)

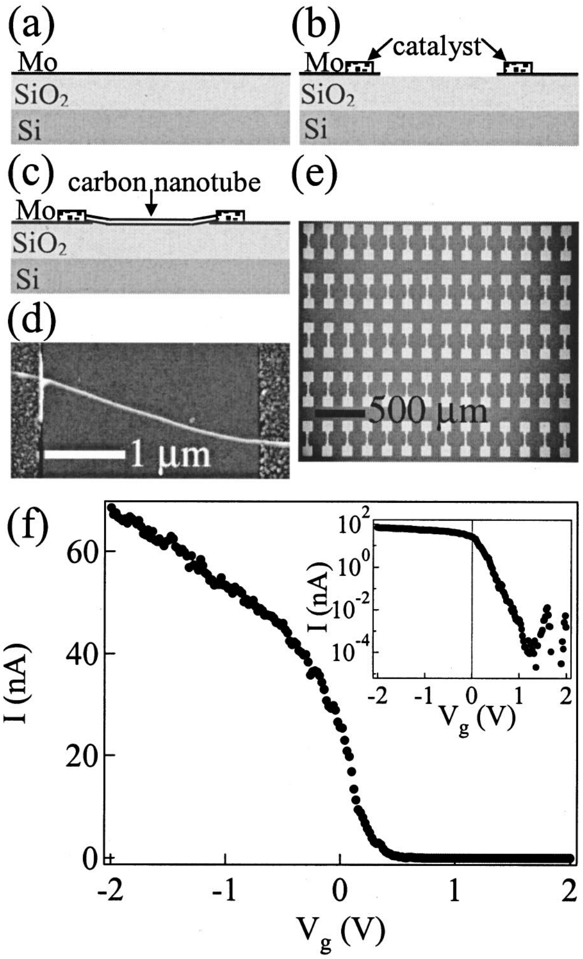

FIG. 3. Growth of SWNTs on flat substrates to bridge preformed Mo electrodes. (a)–(c) schematic process flow. (d) AFM image of a 2.5 nm SWNT grown from one electrode to the opposing one. (e) Optical images of an array of devices. (f) $I-V_g$ of a semiconducting SWNT device thus grown. Bias = 10 mV. The inset shows that the same data in log scale for the current (~6 orders of magnitude difference in conductance for the ON and OFF states).

and 2(e)]. Since Mo coating exists on both the cantilever and the terrace [Fig. 2(a)–2(c)], the bridging nanotube is easily wired up through the opposing Mo electrodes. When bending the cantilever, we observe an increase in the nanotube resistance due to mechanical stretching of the suspended SWNT. Details of this electromechanical property of nanotubes will be presented in a later communication.[16]

The versatility of our tube-growth-between-electrodes approach can be further exploited for facile fabrication of arrays of two-terminal (and multiterminal) nanotube devices on flat substrates (Fig. 3). The atomic force microscope (AFM) image in Fig. 3(d) is taken immediately after CVD, showing a single tube bridging two preformed Mo pads. The nanotube exhibits excellent semiconducting FET characteristics [Fig. 3(f)], with a change of conductance by 6 orders of magnitude [Fig. 3(f) inset] over a gate–voltage span of ~1.5 V (gate oxide thickness 100 nm in this case). The transconductance of the FET is 90 nA/V, and the carrier mobility in the nanotube is calculated to be ~10 000 $cm^2/V\,s$, 20 times higher than the hole mobility in single crystal Si (Ref. 17) at room temperature. This result illustrates that rational substrate design and simple chemical synthesis leads to advanced electronic devices.

The results in this work are obtained with massive arrays of tubes-bridging-Mo devices on substrates as large as a 4 in. wafer. The yields for multiple and individual SWNTs between two opposing Mo electrode are up to 90% and 30%, respectively. Among the individual tubes, the majority of them exhibit semiconducting characteristics. Work is on going to control the number of SWNTs grown from each patterned catalyst island, using well-defined individual iron nanoparticles[18] as catalyst. For the suspended SWNT devices, a fraction of the nanotubes is found to exhibit slack in the suspended lengths, indicating the lack of tension in the suspension. Being able to control the slack and tension will be critical to the resonance frequencies of nanotube "guitar strings" when considering potential applications of nanotube based mechanical resonators. Such control is currently being pursued by manipulation with electric-field directed growth of SWNTs.[19] Progress in controlling nanotube architectures will facilitate the elucidation of nanotube electrical, mechanical, and electromechanical properties and exploitation of useful electrical and nanoelectromechanical systems devices based on nanotube building blocks.

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