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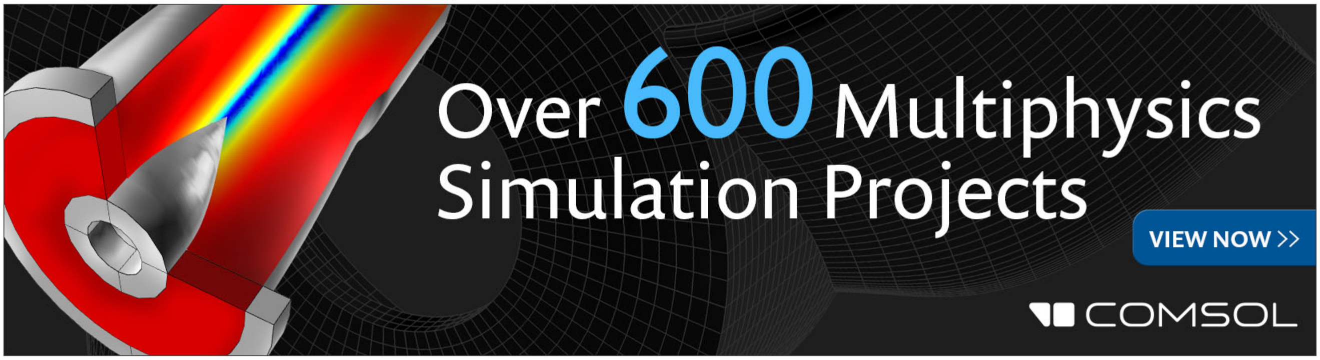

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Self-aligned mechanical attachment of carbon nanotubes to silicon dioxide structures by selective silicon dioxide chemical-vapor deposition

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A self-aligned thin-film deposition technique was developed to mechanically attach carbon nanotubes to surfaces for the fabrication of structurally robust nanotube-based nanomechanical devices. Single-walled carbon nanotubes were grown by thermal chemical-vapor deposition (CVD) across 150-nm-wide SiO_2 trenches. The nanotubes were mechanically attached to the trench tops by selective silicon tetraacetate-based SiO_2 CVD. No film was deposited on the nanotubes where they were suspended across the trenches.
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Single-walled carbon nanotubes (SWNTs) have been shown to possess extraordinary nanomechanical properties,[1] such as a Young's modulus[2] of ~1 TPa and a high aspect ratio. They have been used as cantilever beam flexural oscillators in the megahertz range[2] and as atomic force microscope (AFM) probe tips[3] for high-resolution imaging. Yet, these applications are currently limited by a mechanically weak Van der Waals attraction between the carbon nanotube (CNT) and the substrate. One method,[4] developed to rigidly attach CNTs to AFM probe tips, uses an acrylic adhesive obtained from briefly sticking the probe tip to carbon tape before manually attaching the tube. Another method[5] involves welding a CNT onto a silicon AFM probe tip using a scanning electron microscope (SEM) beam. While each method provides rigid attachment and significantly improves AFM resolution, they are both time consuming and yield CNT probes with inconsistent lengths and diameters.

We are pursuing self-aligned methods for nanomechanical fabrication. Self-alignment is currently a key technology in silicon device manufacturing,[6] and could benefit nanomechanical fabrication processes because

(1) patterned layers can be produced without additional lithography steps and
(2) self-alignment can provide more accurate alignment than lithography.

Additionally, self-aligned methods are useful on three-dimensional structures for which traditional lithography is difficult. For example, self-aligned processes have been useful for defining nanoscale features on AFM probe tips.[7]

We have developed a rigid attachment method to overcome the difficulties of individual CNT attachment, using the self-aligning thin-film deposition technique described here. A CNT was grown over a lithographically produced trench [Figs. 1(a) and 1(b)] and SiO_2 was then deposited over the trench [Fig. 1(c)] to rigidly attach the CNT. The film was deposited selectively on the SiO_2 surface, and did not cover the CNT where it was suspended over the trench. This resulted in a self-aligned attachment of the CNT where it contacted the SiO_2 substrate. If this method had been nonselective, it would have also coated the CNT in the suspended region, increasing its diameter and altering its nanomechanical properties.

The trenches were produced by e-beam lithography in poly(methyl methacrylate) that was spun onto a SiO_2 surface. Dry etching was used to transfer the pattern into the SiO_2, resulting in trenches 150 nm wide and 40 nm deep.

The trenched wafer was dipped into a 150 μg/ml ferric nitrate nonahydrate in isopropyl alcohol catalyst solution.[3] CNTs were then grown on the trench sample by chemical-vapor deposition (CVD) at 700 °C. The CVD was done at atmospheric pressure with flow rates of 150 sccm argon, 100 sccm hydrogen and 5.5 sccm ethylene for 6 min.

The SiO_2 was thermally deposited from a silicon tetraacetate $[Si(O(O)CCH_3)_4]$ precursor in the reaction[8] $Si(O(O)CCH_3)_4(g) \rightarrow SiO_2(s) + 2(CH_3CO)_2O(g)$, which occurs at 170 °C. The $(CH_3CO)_2O$, or acetic anhydride (bp

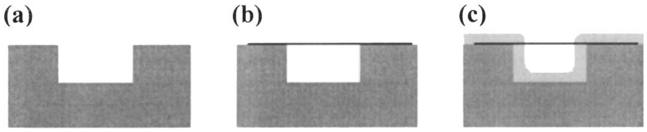

FIG. 1. Self-aligning thin-film attachment method overview. (a) A 40 ×150 nm trench is lithographically produced on a SiO_2 substrate. (b) A CNT is grown over the trench by thermal CVD. (c) The substrate is selectively coated with SiO_2 by a thermal CVD process that does not coat the suspended NT.

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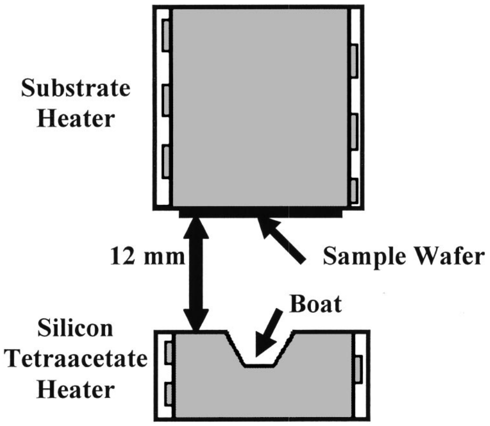

FIG. 2. Heating apparatus for silicon dioxide thermal CVD. The $Si(O(O)CCH_3)_4$ precursor is placed in the lower heater, where it is heated to 100 °C and sublimes. The SiO_2 substrate is placed on the upper heater, 12 mm above the $Si(O(O)CCH_3)_4$, and heated to 170 °C so that the reaction $Si(O(O)CCH_3)_4(g) \rightarrow SiO_2(s) + 2(CH_3CO)_2O(g)$ will occur. A shutter (not shown) separates the two stages. CVD is performed at 120 mTorr.

138–140 °C), is volatile and is not incorporated into the film. The $Si(O(O)CCH_3)_4$ was heated to 100 °C, just below its 111–114 °C melting point, while the CNT–trench sample was held at 170 °C. The pressures at the $Si(O(O)CCH_3)_4$ source and the SiO_2 sample surface were both 120 mTorr. A two-stage heating apparatus (Fig. 2) was specially designed for this CVD process. Each heater was connected to a variable voltage dc power supply and had a thermocouple to monitor temperature. The distance between the wafer substrate and the precursor sample was 12 mm. A shutter separated the wafer substrate and precursor sample, and was removed during deposition. This allowed precise timing of film growth by blocking deposition until the heaters warmed to operating temperature. SiO_2 film thickness was measured by variable-angle spectroscopic ellipsometry (M-2000, J.A. Woollam Co.). X-ray photoelectron spectroscopy (XPS) measurements were performed on an SSX-100 x-ray photoelectron spectrometer with an Al k_α monochromatic source and a hemispherical analyzer.

SiO_2 was deposited on the surface, patterned trench, and CNTs. The sample was examined by a Digital Instruments Dimension 3100 AFM and a Philips XL 30S FEG SEM. NT diameter was determined by measuring height in AFM cross-sectional analysis. Cross-sectional analysis was also used to measure the height difference between the top of the CNT and the top of the grown film. Height measurements are presented without correction for chemical differences between CNTs and SiO_2.

TABLE I. Deposition rate trials for times from 10–40 min. All trials were performed on planar Si substrates, and the $Si(O(O)CCH_3)_4$ precursor was heated to between 97 and 104 °C for all cases. Oxide thicknesses before and after deposition were measured using ellipsometry.

Silicon sample temperature (°C)	Time (min)	Deposited thickness (nm)	Rate (nm/min)
174	10	2.4	0.24
171	10	2.5	0.25
171	15	3.6	0.24
172	30	4.4	0.15
170	40	8.2	0.21
		Avg. rate:	0.22

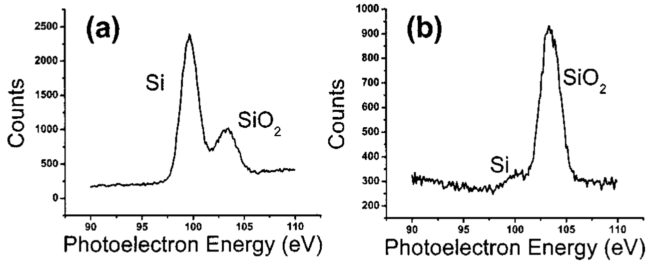

FIG. 3. XPS data of (a) native oxide and (b) deposited oxide. The Si wafer before deposition had spectral peaks characteristic of a native SiO_2 film. After deposition, the wafer showed a significant increase in the strength of the SiO_2 peak, relative to the Si–Si peak. This shows that the deposited layer was SiO_2.

To confirm that SiO_2 films were grown with our CVD apparatus, the SiO_2 was first deposited on planar Si substrates and analyzed. The deposition rate was determined by ellipsometry to be 0.2 nm/min (Table I). Composition and chemical bonding of the deposited film were studied by XPS. Figure 3 shows Si $2p$ XPS narrow scans before and after CVD of SiO_2. The lower binding energy component of these spectra comes from the bulk Si and the higher energy component comes from the Si in SiO_2. The chemical shift of ~4 eV from the bulk Si $2p$ XPS peak is consistent with Si bonded to four oxygen atoms, for example, SiO_2.[9] Prior to SiO_2 CVD, the ratio of Si in SiO_2 to Si in bulk silicon was 0.31. After CVD, this ratio increased significantly to 16. The increase of the SiO_2 peak in relation to the Si peak verified that the deposited layer was SiO_2. The XPS data was also used to calculate the SiO_2 film thickness to confirm the ellipsometry data.[10]

Characterization of deposited films was followed by deposition on suspended CNT samples illustrated in Fig. 1. One of the several CNTs that spanned multiple trenches was found on the trench–nanotube sample by AFM, and landmarks were recorded so that the tube could be located again after processing. The CNT was measured by AFM to be 1.9 nm in diameter (a single-walled CNT), and rested on top of the trenches (Fig. 4). SiO_2 was deposited by CVD on top of

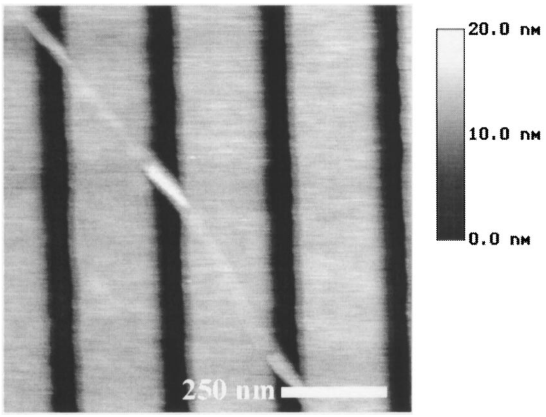

FIG. 4. AFM image of SWNT grown by CVD over trenches in SiO_2. One of the many CNTs found resting on top of the trenches. Landmarks near the NT were recorded so that this specific tube could be located again and studied after SiO_2 deposition. Cross-sectional analysis showed that the NT was 1.9 nm in diameter. Scale bar is 250 nm.

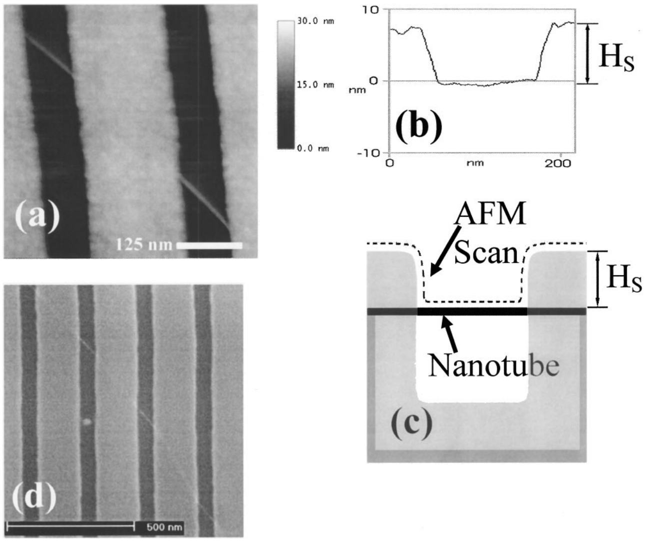

FIG. 5. NT suspended over trench after SiO_2 deposition. (a) AFM height image. (b) Coaxial line scan of NT buried in SiO_2 and suspended over trench from image in part (a) yielded a step height H_S of 8.2 nm. (c) Schematic diagram showing the path for the line scan in (b). (d) SEM image.

the trenches and CNTs for 55 min at 172 °C. The sample was then imaged with AFM [Fig. 5(a)]. AFM height measurements showed a difference of 8.2 nm between the top of the NT and the top of the trenches [Figs. 5(b) and 5(c)]. This height difference shows that a film covered the NT where it was in contact with the substrate, but that very little or no film was deposited on the suspended region of the tube, confirming that we achieved selective SiO_2 deposition. The SEM image in Fig. 5(d) shows both the covered and suspended segments of the NT under the deposited film.

The selectivity of the deposition is consistent with the expected surface chemistry. While the CNT, graphene surface should be chemically inert to $Si(O(O)CCH_3)_4$, surface silanols ($\equiv$SiOH) of the patterned trench tops should readily react with $Si(O(O)CCH_3)_4$ to form acetic acid ($HOC(O)CH_3$) and $\equiv SiOSi(O(O)CCH_3)_3$. This is the start of the chemisorbed SiO_2 layer, which continues to grow according to the previously mentioned reaction $Si(O(O)CCH_3)_4(g) \rightarrow SiO_2(s) + 2(CH_3CO)_2O(g)$, at 170 °C.

Silicon tetraacetate-based SiO_2 CVD provides a self-aligned method to rigidly attach CNTs to SiO_2 structures. Other oxide structures could also be compatible with this process, and should be explored. The self-aligned nature of the process will allow rigid NT attachment on three-dimensional SiO_2 structures such as AFM probe tips. This process is compatible with mass fabrication of CNT AFM probes and could aid in making them available to a wider range of researchers. This process may be particularly valuable for producing CNT AFM tips for fluid imaging, where rigid attachment to the tip is critical.

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