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ALD of High-κ Dielectrics on Suspended Functionalized SWNTs

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Conformal atomic layer deposition (ALD) on as-grown suspended single-walled carbon nanotubes (SWNTs) is not possible due to the inertness of ALD precursor molecules to the SWNT surface. Here, we present a functionalization technique that makes SWNTs reactive with ALD precursors, and deposit high-κ oxides (Al_2O_3 and HfO_2) onto the nanotubes to illustrate this method. Reactivity of the precursors with the functionalized nanotubes is due to -NO_2 functional groups attached to the nanotube sidewalls. The effect of the functionalization on the nanotube conductance is shown to be reversible, and doping caused by the deposited oxides is discussed.

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Many of the promising applications that exploit the unique properties of suspended single-walled carbon nanotubes (SWNTs), such as surround-gate[1] transistors with large charging energies,[2] will only be achievable if the nanotubes are surrounded by a protective passivation layer. The extreme sensitivity of SWNTs to their chemical environment is well documented, and is a major obstacle in the field of nanotube device fabrication.[3-5] SWNTs coated with both metallic[6] and superconducting[7,8] materials have been demonstrated to produce interesting phenomena, but such coatings do not preserve the electronic properties of the nanotubes. Encasing SWNTs with insulating material is therefore highly desirable. This has been previously demonstrated using chemical vapor deposition (CVD).[2,9] However, many disadvantages exist that are inherent to CVD, including film nonuniformity and high temperature, which increases contact resistance.[10] Liquid-chemical deposition methods have also been used to coat SWNTs with SiO_2,[11,12] a low-κ dielectric, but this approach has not been adapted for the deposition of higher-κ materials.

Atomic layer deposition (ALD) on SWNTs is of interest because it allows for the deposition of a wide variety of materials at relatively low temperatures with superior thickness precision and high composition uniformity.[13] Conformal ALD coating around multiwalled carbon nanotubes (MWNTs) is a straightforward and highly reproducible process.[14] The same, however, cannot be said about SWNTs, which are chemically inert to ALD precursor molecules. As a result, continuous ALD coating is impossible to achieve without the assistance of a supporting substrate onto which the material can be deposited (substrate-assisted growth).[15,16] The benefit of this chemical inertness is that it allows for the creation of a totally benign dielectric/nanotube interface that does not adversely affect the electrical properties of the nanotube. In fact, this property has been shown to be crucial for the fabrication of SWNT field effect devices that exhibit ballistic transport at room temperature.[16] A drawback of this chemical inertness is that it requires ALD fabrication techniques to rely on substrate-assisted growth, which adds a constraint to SWNT device design. For instance, in substrate-assisted growth, ALD coatings go only part way around the nanotubes, so the fabrication of surround-gate SWNT devices cannot be achieved. Suspended nanotube geometries are needed for such devices to be realized, which means that the SWNT inertness must be overcome. It is therefore desirable to establish a functionalization technique that not only makes SWNTs reactive with gas-phase ALD precursor molecules, but also allows the nanotubes to retain their electrical properties. We describe such a technique here, and show its effect on electrically contacted suspended SWNTs and SWNT bundles.

In our experiments, suspended SWNT samples were fabricated using optical lithography, electron beam evaporation, and lift off processing to pattern a several micrometer wide metallic line (Pt 50 nm/Ti 5 nm) onto a 200 nm thick self-supporting Si_3N_4 membrane. A focused ion beam (FIB) was used to mill a 1 μm wide slit through the line and the supporting Si_3N_4 underneath. The newly separated halves of the metallic line served as two addressable electrodes separated by the 1 μm wide gap. Fe catalyst (1.6 nm) was evaporated onto the substrate surface for CVD nanotube growth, which was carried out at 900°C in a flowing CH_4 atmosphere (200 sccm) for 5 min.[17] During growth, one or several SWNTs made themselves electrically accessible by growing over the gap and bridging the two electrodes (Fig. 1a).[18] Agglomeration of the Pt occurred at this temperature, which limited the number of current pathways through the patterned line, and thus limited the number of SWNTs that were electrically contacted.

A flow-through style ALD reactor[19] was used to make two different high-κ oxides for this study: Al_2O_3 ($\kappa \approx 8$) and HfO_2 ($\kappa \approx 16$). The metal sources used for Al_2O_3 and HfO_2 were trimethylaluminum and tetrakis[diethylamino]hafnium, respectively. H_2O was used as the oxygen source for both materials, and 225°C was the deposition temperature used in both cases. 10 nm of either oxide was deposited onto the as-grown nanotube samples. The purpose of this ALD step was twofold. While it left the main body of the suspended nanotubes bare, it helped to anchor them to the supporting substrate by growing up and around the segments that were in contact with the Si_3N_4 membrane. This limited the lateral motion of the nanotube, ensuring that it stayed attached during the liquid-chemical functionalization treatment that followed (Fig. 1b). This initial ALD step also coated any existing non-SWNT structures, guaranteeing that SWNTs were the only current carrying species that could take part in the chemical treatment.

Chemical functionalization was carried out with *in situ* generated diazonium compounds.[20] The samples were submerged in solutions consisting of 10 mL 1,2-dichlorobenzene, 5 mL acetonitrile, and 2.6 mmol of an aniline derivative. In these experiments, two types of aniline derivatives were used for comparison purposes: aniline and nitroaniline. The solutions were sealed and bubbled for 10 min with nitrogen, and heated to 60°C. 4.0 mmol of isoamyl nitrite was then quickly added to generate the reactive species, and the samples were allowed to sit in this solution for at least 15 h to ensure reaction completeness. During functionalization, the reactive diazonium species were covalently bonded to the SWNT sidewalls (Fig. 1c). A series of dilutions were then used to clean the samples. Copious amounts of dimethylformamide were first added until the solution was clear. This was followed by extensive dilutions in diethyl ether and high purity hexanes, respectively. To determine if the functionalization succeeded in making the SWNTs more susceptible to ALD reactions, an additional 10 nm of ALD oxide was deposited onto the samples (Fig. 1d).

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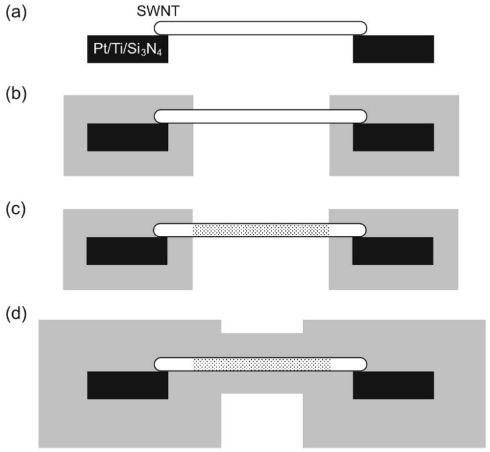

Figure 1. Schematic cross-section of the sample processing steps. (a) SWNTs are grown across a gap in the supporting Si_3N_4 membrane. (b) ALD oxide is deposited onto the sample, but does not grow on the inert SWNTs. (c) The liquid chemical treatment is carried out, which functionalizes the exposed portion of the SWNTs. (d) A second ALD run is performed, which uniformly coats the functionalized SWNTs.

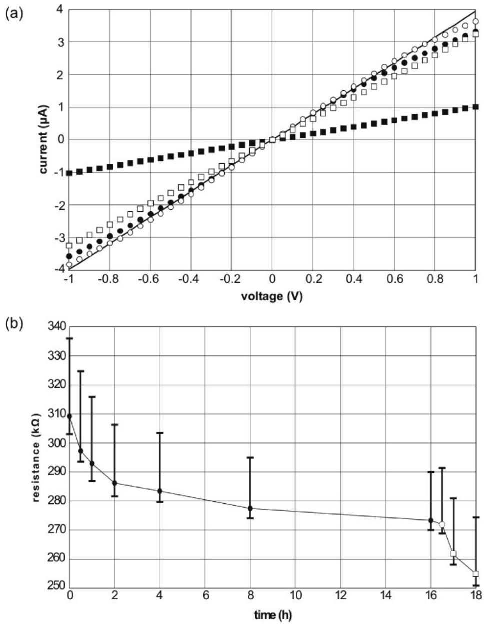

Figure 3. (a) Current-voltage analysis of suspended SWNTs. The conductance of the as-grown SWNTs (filled circles) after 10 nm HfO_2 deposition increases (open circles). Functionalization results in a substantial conductance decrease (filled squares). An additional 10 nm of HfO_2 results in a conductance increase (open squares), and subsequent annealing results in a further conductance increase (solid line). (b) In a more detailed study of the annealing behavior, the room temperature *ex situ* resistance is shown to decrease exponentially with annealing time. 300°C (filled circles), 325°C (open circle), 350°C (open squares).

The fact that the SWNTs were suspended over a gap made them ideal structures for transmission electron microscopy (TEM) studies. The TEM images in Fig. 2 compare Al_2O_3 coated SWNTs functionalized using the two different aniline derivatives. In both cases, the functionalization resulted in the attachment of aryl ligands to the nanotube sidewalls. It is clear from these micrographs, however, that only SWNTs functionalized using nitroaniline result in conformal coating. The aniline treated SWNTs produced structures that are similar in appearance to as-grown ALD coated SWNTs, exhibiting purely localized oxide nucleation (Fig. 2a). However, ALD oxide spheres on as-grown SWNTs are typically the same size and concentric around the nanotube,[16] while the oxide spheres on aniline treated SWNTs are not. This may be the result of steric hindrance caused by the attached ligands, which can temporarily obstruct precursor molecules from reactive sites on the nanotube surface. Such a mechanism could cause various degrees of nucleation inhibition, resulting in oxide spheres of different sizes. Unlike their aniline treated counterparts, SWNTs functionalized using nitroaniline exhibit Al_2O_3 coating that is strikingly uniform and continuous. The encased SWNT (Fig. 2b) can be adequately resolved through the oxide layer, and had a diameter of 2 nm. The diameter of the oxide nanorod after 100 ALD cycles is 22 nm, which corresponds well with the established growth rate of 0.1 nm/cycle for Al_2O_3. In other words, SWNTs functionalized using nitroaniline showed little if any inhibition of nucleation. These results show that the nitro functional group specifically facilitates reaction with the gas-phase ALD precursor molecules. This type of reaction is common in organometallic chemistry,[21] and illustrates the importance of appropriate ligand selection when functionalizing SWNTs for ALD coating purposes.

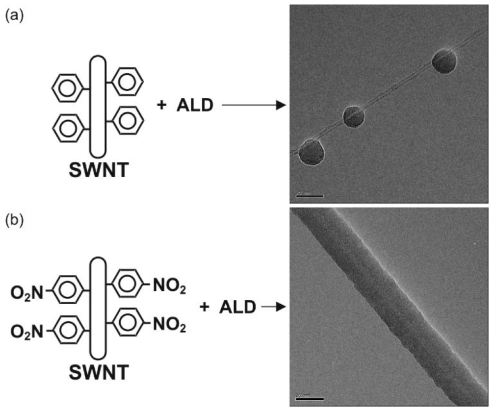

Figure 2. Reaction schematic with TEM results of functionalized suspended SWNTs exposed to 100 ALD cycles of Al_2O_3. (a) SWNTs functionalized using aniline exhibit localized ALD nucleation. The Al_2O_3 spheres here measure 15, 17, and 20 nm. (b) SWNTs functionalized using nitroaniline exhibit continuous ALD coating. The diameter of the Al_2O_3 wire is 22 nm. (Scale bar: 20 nm).

Room-temperature current-voltage (IV) measurements of suspended SWNTs functionalized using nitroaniline and coated with HfO_2 were made in between the different stages of sample processing (Fig. 3a). The IV curve of the as-grown SWNT is slightly nonlinear, corresponding to a nanotube with semiconducting properties.[22] The slope of the curve slightly increases after the initial ALD step, indicating a slight conductance increase. It has been previously demonstrated that individual semiconducting SWNTs generally exhibit p-type behavior.[3,23] This suggests that the presence of the oxide at the metal/nanotube junction is effectively doping those regions to have a greater p-type character. High-frequency capacitance-voltage (CV) analysis of our HfO_2 thin films supports this assertion. The CV curves exhibit flatband voltage shifts to more positive values, which is indicative of negative charge trapping in the oxide.[24] In other words, the metal centers of the HfO_2 at the metal/nanotube junction are functioning as electron traps, the overall result being stronger p-type behavior.

Chemical functionalization has the opposite effect on the SWNT conductance properties, causing a dramatic resistance increase. This is to be expected considering that the SWNT is initially in a sp^2 hybridized electronic state, and the ligand attachment converts the nanotube into the more resistive sp^3 configuration.[20] This type of resistance increase is well documented, and has been observed in both carbon films and functionalized carbon nanotubes.[25,26]

Partial recovery of the conductance was attained in the second

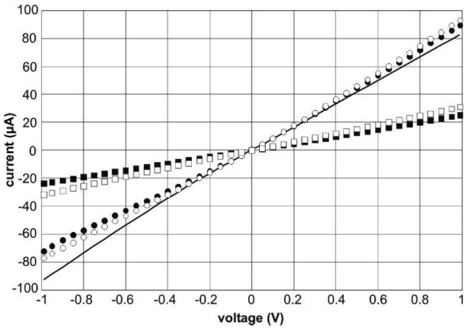

Figure 4. Current-voltage characteristics of SWNT bundles. Al_2O_3 ALD is used instead of HfO_2, but the conductance trends are identical to what was found in the suspended SWNT case. The conductance of as-grown SWNTs (filled circles) increases after 10 nm of Al_2O_3 deposition (open circles). Chemical functionalization (filled squares) causes a conductance decrease. Another 10 nm Al_2O_3 deposition results in a conductance increase (open squares), while additional conductivity is attained after a 600°C anneal for 1 h (solid line).

ALD step, where the bare but now functionalized segments of the SWNT are coated with HfO_2. This led to the same doping trend observed in the initial ALD step. In this case, however, two mechanisms were probably responsible for the conductance increase. First, Hf centers that serve as electron traps now existed along the entire length of the SWNT, causing an enhancement in the p-type character as before. In addition, thermogravimetric analysis from previous work has shown that these particular attached ligands can be cleaved from the nanotube at elevated temperatures.[27] A detectable weight decrease can be observed starting at a temperature of 250°C, which is close to the ALD deposition temperature used in these experiments (225 ± 5°C). Considering that the entire deposition takes several hours, it is possible that a portion of the attached ligands were dissociating from the nanotube sidewalls during the deposition process. This would result in a conversion back to a sp^2 hybridized state in the areas of dissociation, and a corresponding resistance decrease in those areas. However, the fact that the SWNTs could be uniformly coated under these deposition parameters suggests that the amount of ligand cleavage is not extensive before the first several monolayers of oxide can react with the functional groups.

Anneals in an inert argon atmosphere were performed to achieve complete ligand cleavage along the entire nanotube length, effectively restoring the SWNT to its original hybridization state and corresponding conductive properties. It can be seen (Fig. 3b) that the resistance decreased exponentially with annealing time, signifying ligand dissociation. The mean lifetime of the attached ligands at 300°C has been calculated from the data to be ~96 min ($R^2 = 0.9$), which is more than three times higher than reported for functionalized, uncoated nanotubes. This may be due to a caging effect caused by the surrounding HfO_2 layer. Such an arrangement can increase the stability of the ligands on the nanotube sidewalls, making the dissociation rate slower compared to the rate on uncoated nanotubes. Anneals at 325 and 350°C caused further resistance decreases at faster rates. Proper combination of annealing time and temperature resulted in the full recovery of the SWNT conductivity.

The suspended SWNT results were supported by experiments done on SWNT bundles. Bundled SWNT samples were fabricated in a similar fashion with the exception that the nanotubes were grown at a temperature of 800°C. The lower growth temperature avoids the Pt agglomeration that occurs at 900°C, thereby increasing the number of SWNTs that are electrically accessible both over the gap and between much wider electrodes that are connected in parallel. ALD Al_2O_3 was used instead of HfO_2 for the bundled SWNT experiments. Like HfO_2, the metal centers in Al_2O_3 are known to trap negative charge, so a conductivity increase upon deposition was expected. The IV results confirm this (Fig. 4), showing a slight increase in conductivity after the initial 10 nm were deposited. Chemical functionalization caused a decrease in conduction through the bundle, as expected, and the subsequent Al_2O_3 deposition resulted in another small conduction increase. Finally, a 600°C anneal in argon for 1 h restored the bundle's conductivity close to its initial value. The magnitudes of the conduction changes were different because the bundle consists of many nanotubes with varying degrees of conductivity, but the trends mirror what was observed in the suspended SWNT case.

In summary, conformal coating of suspended single-walled carbon nanotubes with high-κ dielectric materials has been achieved using atomic layer deposition. The change in the electrical properties due to the functionalization technique employed has been shown to be reversible, which is crucial for attaining room temperature ballistic transport through insulator-coated nanotubes. It is anticipated that this technique will have a significant impact in many SWNT device applications, including SWNT devices with ultrathin dielectrics and surround-gate structures.

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