Unique Mechanical Properties of Carbon Nanotube Film-Solid State Interfaces

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If the surface of a mechanical resonator is coated with a film of carbon nanotubes, one might expect that the quality factor (Q) of the resonator would be degraded, because the motion of the tubes scraping over both each other and the resonator surface would add friction. That just the opposite is the case was discovered with recent research in carbon nanotube films with thicknesses of 100 to 1000 nm deposited on a variety of resonators. The Q's of the resonators increased by as much as a factor of six for some normal modes. It is believed that the increase is caused by the reinforcement of surface microcracks by the axially strong nanotubes.

Mechanical resonators are integral components of a vast array of devices and technologies. Large resonators have been used to detect gravitational waves [1] while small quartz resonators are used to keep time in a wrist watch. With the explosion of micro-electro-mechanical systems (MEMS), many devices may now be mass produced on much smaller length scales, reducing cost, packaging size, and power consumption. A large class of practical devices, including gas sensors, high frequency electronic filters, and gyroscopes, are based on small mechanical resonators and, as will be discussed later, the precision of these instruments is determined by the quality factor (Q) of the resonance peak. Energy dissipation in solid resonators can be caused by many physical processes, including thermoelastic effects, phonon-phonon interactions, and internal crystal defects. For small MEMS scale resonators, which have relatively large surface area to volume ratios, losses due to surface effects can become a significant contributor [2]. One would expect that adding a foreign system, such as a fibrous coating, to the surface of a small resonator would add avenues of energy dissipation, and would reduce the Q of the resonator. However, we have recently discovered that a tangled mat of carbon nanotubes in a thin coating on the surface of a small resonator can dramatically increase the Q, by a factor of six in some cases. In this Letter we report these observations for carbon nanotube films with thicknesses of 100 to 1000 nm deposited on a variety of substrates, and suggest an explanation for the increased Q.

Carbon nanotubes (CNTs) are a unique morphology of carbon quite different than the typical natural forms of diamond and graphite [3–5]. Nanotubes can be visualized as a hexagonal graphene sheet of carbon atoms which has been rolled into a seamless cylinder. A single wall carbon nanotube (SWNT) is a single such cylinder with diameter ∼1.5 nm and length up to tens of microns. The covalently bonded carbon network produces an extremely strong structure, arguably the strongest in nature. The axial Young's modulus has been obtained experimentally by several means[6, 7], as well as calculated theoretically [8], and is typically found to be between 1 - 1.8 TPa.
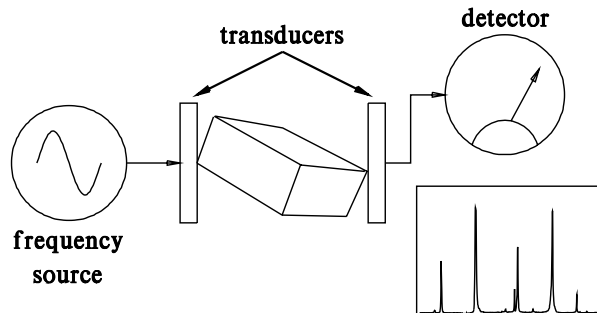

FIG. 1: The SWNT film is deposited on a large surface of a polished substrate and mounted on diametrically opposed corners between two thin piezoelectric transducers. The sample is excited by sinusoidal vibrations of one transducer and the sample response is monitored by the other. The output signal is recorded by a high frequency lock-in amplifier, producing a spectrum like that shown in the inset.

These unique mechanical properties, along with equally interesting electronic properties, have prompted massive efforts in diverse scientific communities, and hundreds (if not thousands) of proposed applications [9–12]. A comprehensive review of CNTs has been compiled by M.S. Dresselhaus, G. Dresselhaus, and Ph. Avouris [13]. Our Letter presents experiments designed to investigate the interaction between a mat of nanotubes and a supporting substrate surface, with the goal of examining the effect on the quality factor and natural frequencies of small mechanical resonators. It was discovered that CNT films between 400 - 600nm thick can increase the quality factor of solid resonators by as much as a factor of six.

The Q of a low loss resonator is typically measured as the ratio of the natural frequency to the width of the resonance peak. A high Q resonance peak is narrow, thus sharply defining the resonance frequency and enabling more precise detection of small shifts in that natural frequency. In these experiments, we characterize the lowest 15-20 mechanical resonance frequencies and Q's for a variety of solid-state resonators, then deposit thin films of SWNTs and examine the changes in the results. Films
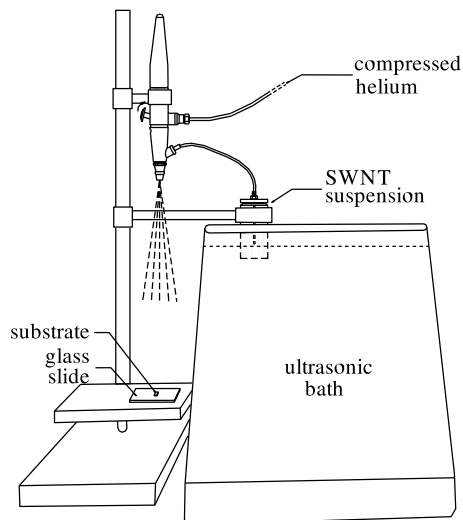
FIG. 2: The airbrush aparatus used to deposit the SWNT films. The low power ultrasonic bath is used to keep the suspension well mixed during deposition.

substrate	Q_{bare}	Q_{film}	ratio	d(nm)	mode
Alumina	2343	13355	5.70	400	3
STO 1	5917	12175	2.06	400	15
STO 2	6071	13357	2.20	500	16
STO 3	5389	32334	6.00	200	6
Silicon	1827	3043	1.67	600	15
Quartz	1996	8725	4.37	200	6
Brass (rough)	1324	2352	1.78	400	8

TABLE I: Modes exhibiting the largest increase in Q for various substrates, where d is the film thickness. The STO entries are for three different strontium titanate samples. All sample surfaces were prepared with 0.5 μm diamond paper polishing except the brass which was roughly polished with emery paper.

ranged in thickness from 100 to 1,000 nm and resonators consisted of various diverse materials polished into quite accurate parallelepipeds with dimensions between ~ 200 to 750 μm. The substrate materials used were single crystal silicon, strontium titanate (STO), quartz, and alumina (saphire), as well as the alloy brass. The general procedure is as follows. A sample is cut with a diamond wire saw and polished with 0.5 μm diamond paper to a mirror finish (an exception was the brass which was only roughly shaped with emery paper). An atomic force microscope (AFM) was used to characterize the surface roughness of silicon, alumina, and strontium titanate polished surfaces, quantified by the RMS deviation of surface height over a prescribed area. Our polishing methods consistently resulted in about 3nm roughness over most of the surface, with occasional larger scale cracks and defects, for each of the materials tested.

The polished sample is very lightly mounted on diametrically opposed corners between two transducers, as illustrated in Fig. 1 [14, 15]. Vibrational modes are excited in the sample by applying a sinusoidal voltage to one of the transducers and sweeping through a range of frequencies. The sample response is monitored by the opposing transducer connected to a high frequency lock-in amplifier, and digitally recorded. The resulting resonance peaks in the spectrum can be fit with a Lorentzian lineshape so that the center frequency and quality factor can be precisely extracted. For reference, frequency ranges for the lowest ~ 20 modes are typically 0.6 to 5 MHz, and typical quality factors for bare substrates are 1,000 to 10,000 and are material and mode dependent. After the first 15-20 normal modes of the bare substrate have been obtained, the sample is removed from the cell and a SWNT film is deposited.

The transducers supporting the sample also provide another mechanism for energy loss and since the sample must be removed from the resonance apparatus for film deposition, it is important to know how reproducible the Q measurements are upon remounting. We conducted a statistical study in which a particular sample of strontium titanate was repeatedly mounted 25 times by two different experimenters. It was found that the variance in the Q measurements is about 10% and the frequency is about 75 ppm. During the SWNT film thickness experiments, care was taken to remount the sample in the same orientation and by the same experimenter without removing the cell from the mounting apparatus.

The raw carbon nanotubes are fabricated by the arc discharge method and consist of single wall nanotubes aggregated into bundles. The as-prepared SWNT sample is purified using a HCl acid bath process until the resulting powder is about 70% SWNT by weight [16]. This purification step was found to be important for these experiments. The powder is ultrasonically dispersed in ethanol for about 15 minutes with a concentration of 2 mg of SWNT powder to 15 mL of ethanol. An artists air brush, as shown in Fig. 2, using helium as the compressed gas source, is used to spray short (~ 1 sec) bursts of the suspension on the substrate, followed by a slightly longer burst of dry helium to quickly evaporate the ethanol. The process is repeated until the desired film thickness is achieved. An AFM was used to measure the film thickness for a range of numbers of bursts, and a linear relation, with free intercept of very nearly zero, was found. This deposition method reliably produced visually uniform films with thicknesses ranging from 100 to 1,000 nm. Initial samples were then baked under high vacuum at a temperature of $500°$C for about 24 hours to drive off contaminants such as water vapor and oxygen trapped in the nanotube mat. This degassing step affected our results by only 5-10% and so was omitted for the data presented here. Finally, the sample was remounted in the resonance cell and a new spectrum obtained, from which
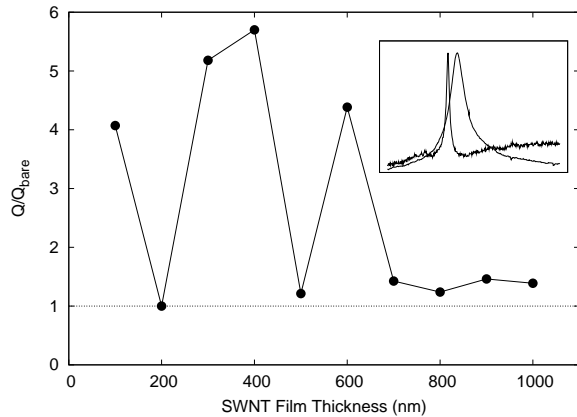
FIG. 3: The change in the quality factor for mode 3 of the alumina substrate with SWNT film thickness. The uncertainty in the Q measurements due to remounting is about 10%. The inset shows a resonance peak for the alumina sample with (darker line) and without (lighter line) a 400 nm SWNT film. With the application of the SWNT film, the Q has increased by a factor of 5.70.
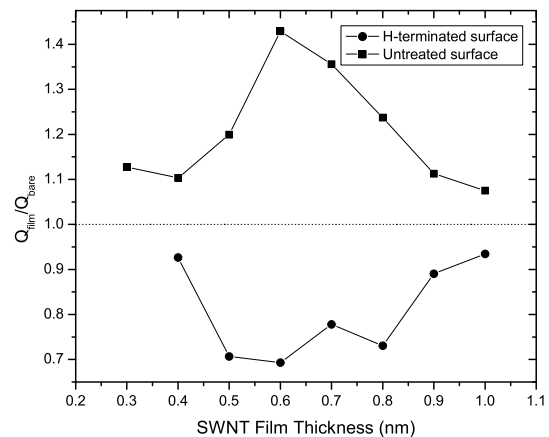

FIG. 4: The quality factor response, averaged over the first 15 modes, for a polished silicon sample (squares) and after passivating the dangling surface bonds with hydrogen (circles).

changes in the Q were determined.

Upon comparing the natural frequencies of a sample before and after film deposition, all of the samples show a monotonic decrease in frequency with thicker films for all modes. As an example, a 500 nm film on strontium titanate substrate resulted in natural frequency reductions ranging from 50-500 parts per million (ppm) depending on the mode. We attribute these shifts to the mass loading of the resonator by the film, just as a mass-spring system will decrease in natural frequency with increasing mass. More interesting however is the the effect on the quality factor. As mentioned above, the quality factor is an indicator of the damping, or energy dissipation, in the resonator. In general, when a film is added to a resonator, the quality factor almost invariably decreases because more avenues for energy dissipation are available to the system including internal friction in the film and the film/substrate interface. In fact, this is precisely why strict cleanliness protocols are required when fabricating high Q resonators [2]. However, we were surprised to find the effect of the carbon nanotube films was to *increase* the quality factors for all the substrates tested by factors as high as 6.0. Not surprisingly, the magnitude of the effect is different for different modes. Table 1 lists those modes exhibiting the largest increases. Somewhat counterintuitively, we could find no correlation between the strongly effected modes and the particular motion of the surface containing the nanotube film.

The effect on the quality factor as function of film thickness was explored by taking spectra at intervals of 100 nm in deposited film thickness. Representative results for the relative increase in Q for mode 3 of the

alumina sample are shown in Fig. 3. The inset illustrates a factor of 5.7 increase in the Q for the film thickness of 400 nm. It is worth noting that the quality factors for all polished single crystal materials increased most significantly for film thicknesses between 400 and 600 nm, while the roughly shaped brass showed no such film thickness dependence. The modes most strongly affected by the presence of the CNT films are listed in Table . As a control experiment, we deposited films of high surface area carbon soot (containing no SWNTs) in precisely the same way, and found the Q dropped on average by a factor of about 0.75.

In an effort to better understand this phenomenon, we passivated the surface of the silicon sample through a chemical etching process consisting of a 10 minute exposure to dilute HF acid (1.6%) followed by boiling in distilled water for 30 minutes. Such a procedure has been shown to remove the native oxides from the silicon surface and terminate the surface bonds with hydrogen [17]. SWNT films were then deposited in the same way with thicknesses ranging from 400 to 1,000 nm. Not only did the passivated Si surface reduce the Q enhancing effect of the SWNTs, but exhibited the *excess* losses (factor of 0.7 reduction of bare substrate Q's) typical in a film/substrate system as we had originally expected (see Fig. 4).

The observations above may be explained by considering the energy loss mechanisms confined to surfaces. All surfaces contain an array microcracks and defects, the density and severity of which are dependent on the surface preparation procedures and material. For small samples such as these, with relatively large surface area to volume ratios, the surface losses can be a significant fraction to the overall dissipation. Surface cracks may
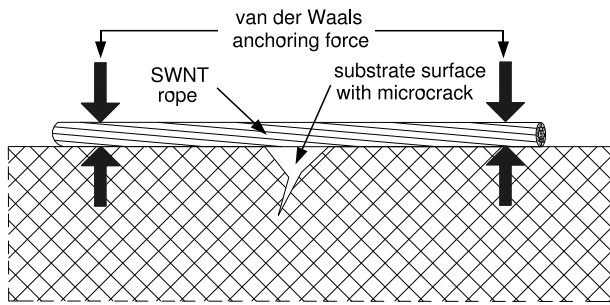
FIG. 5: Model for the reinforcement of a surface microcrack in a substrate by a SWNT bundle.

increase the efficiency of small mechanical resonators. While we have observed increases in the quality factor of resonators as high as factors of 6, we are certain that the film deposition and surface preparation techniques are far from optimized; and much larger increases may well be realized. Such optimization steps might include designing a more controlled film deposition process, functionalizing the SWNTs to interact more strongly with the surface, and devising a method of depositing the films without removing the substrate from the resonance apparatus. With the rapid development of solid state MEMS devices using mechanical resonators, thin CNT coatings could increase the precision of these instruments, opening up new markets and applications.

dynamically open and close during a resonance cycle producing non-linear effects, and such effects produce higher frequency spectral components, thus channelling energy away from the coherent vibrations at the resonance frequency. We believe that the axially stiff carbon nanotubes positioned over these cracks, as illustrated in Fig. 5, provide reinforcement so that the lateral motion of the crack edges is greatly reduced. This produces the suppression of surface losses seen in the bare resonator. Clearly, this model requires that a significant portion of the tube length is well anchored to the sample surface. By passivating the surface of the silicon with hydrogen atoms, we weakened the tube/surface interaction to such a degree that the tubes were most likely sliding on the surface, robbing energy from the system through friction.

If the tubes were well aligned so as to maximize the area of interaction between the tubes and substrate surface, the most efficient suppression of the surface losses should occur with only a few monolayers of SWNTs. This would supply the reinforcement, but minimize the internal friction losses within the film itself. However, our tubes form a randomly oriented mat so that to obtain a sufficient percentage of the surface interacting with the CNTs, thicker films may be required. As the film grows thicker ($> \sim 600$nm), no further suppression of surface losses results and internal friction, both within the film and at the film/substrate interface, begins to play a more dominant role. This picture qualitatively explains the dependence of loss suppression on CNT film thickness.

These experiments have illustrated yet another remarkable property of carbon nanotubes, the ability to

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