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Nonhomogeneous morphology and the elastic modulus of aligned carbon nanotube films

Yoonjin Won^{1,2}, Yuan Gao², Roberto Guzman de Villoria^{3,5}, Brian L Wardle³, Rong Xiang^{4,6}, Shigeo Maruyama⁴, Thomas W Kenny² and Kenneth E Goodson²

¹ Department of Mechanical and Aerospace Engineering, University of California, Irvine, Irvine, CA 92697, USA

² Department of Mechanical Engineering, 440 Escondido Mall, Stanford University, Stanford, CA 94305, USA

³ Department of Aeronautics and Astronautics, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

⁴ Department of Mechanical Engineering, The University of Tokyo, Tokyo 113–8656, Japan

⁵ Madrid Institutes for Advanced Research, Madrid, Spain

⁶ School of Physics and Engineering, Sun Yat-sen University, Guangzhou 510275, People's Republic of China

E-mail: yunjin.won@gmail.com

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Abstract

Carbon nanotube (CNT) arrays offer the potential to develop nanostructured materials that leverage their outstanding physical properties. Vertically aligned carbon nanotubes (VACNTs), also named CNT forests, CNT arrays, or CNT turfs, can provide high heat conductivity and sufficient mechanical compliance to accommodate thermal expansion mismatch for use as thermal interface materials (TIMs). This paper reports measurements of the in-plane moduli of vertically aligned, single-walled CNT (SWCNT) and multi-walled CNT (MWCNT) films. The mechanical response of these films is related to the nonhomogeneous morphology of the grown nanotubes, such as entangled nanotubes of a top crust layer, aligned CNTs in the middle region, and CNTs in the bottom layer. To investigate how the entanglements govern the overall mechanical moduli of CNT films, we remove the crust layer consisting of CNT entanglements by etching the CNT films from the top. A microfabricated cantilever technique shows that crust removal reduces the resulting moduli of the etched SWCNT films by as much as 40%, whereas the moduli of the etched MWCNT films do not change significantly, suggesting a minimal crust effect on the film modulus for thick MWCNT films ($>90\text{ }\mu\text{m}$). This improved understanding will allow us to engineer the mechanical moduli of CNT films for TIMs or packaging applications.

Keywords: carbon nanotubes, CNT forest, CNT array, CNT film, mechanical modulus, morphology, thermal interfaces

(Some figures may appear in colour only in the online journal)

1. Introduction

In electronic components, it is crucial to minimize the thermal resistances between the heat sink and heat spreader by minimizing air gaps. The surface roughness of planar surfaces

limits the actual contact area between the two solids to values as low as 2% for lightly loaded interfaces [1]. These components also experience repeated temperature cycles that cause mechanical stresses at the interface between the two different materials. Therefore, mechanically compliant thermal

interface materials (TIMs) are used to join surfaces to improve heat transfer across the interface and minimize the effects of thermomechanical mismatch. Here, vertically aligned carbon nanotube (VACNT) films have been proposed as ideal TIMs due to their ability to combine the mechanical compliance of a polymer with the high thermal conductivity of a metal [2–7].

While the out-of-plane elastic modulus has been studied using nanoindentation [1, 8], there is limited data for the in-plane elastic modulus (perpendicular to the primary direction of the carbon nanotubes (CNTs)). Past nanoindentation experiments have produced estimates of the out-of-plane (CNT axis direction) modulus ranging from 1 to 300 MPa as a result of nanotube morphology variations [2–11]. Our past results using nanoindentation measurements show that out-of-plane modulus of multi-walled CNT (MWCNT) films ranging from 0.2 to 2.8 MPa [8]. These results suggest that the overall density, roughness, array height, and other physical characteristics may strongly influence the mechanical properties of VACNT films. Previous measurements of the in-plane modulus of VACNT films also suggested that the wide distribution of modulus values stem from the variation of nanostructural features [12, 13]. The nonhomogeneous characteristics of VACNT films have been confirmed by several studies using various types of measurements, such as scanning electron microscopy (SEM), resonant Raman spectroscopy, and angle-resolved x-ray absorption [14–18]. Therefore, it is critical to relate the mechanical properties of VACNT films to variations (effectively this is spatial heterogeneity) in the morphology of the nanotube films. In recent work, we have investigated the mechanical compliance of single-walled CNT (SWCNT) films, and the mechanical responses are linked to their morphology and microscopic motions, including zipping, unzipping, and entanglements [19]. Performance of TIM materials as well as other VACNT-comprised structures [20, 21], particularly those used in microfabrication, will be directly affected by such structure-property heterogeneity, e.g. bioparticle separation elements and 3D structures formed via capillary infiltration of fluids into patterned arrays are likely very sensitive to such spatial heterogeneities [22–24].

In this paper, a resonator technique is used to infer the in-plane modulus of vertically aligned SWCNT and MWCNT films using a laser Doppler vibrometer (LDV) to ascertain resonance shifts. We additionally investigate the modulus after removing the crust from the VACNT films using plasma etching to understand those local morphological effects on the overall mechanical responses.

2. Methods

2.1. Materials

Figure 1 shows the suggested mechanical characterization method before and after the etching step using a Si-CNT composite beam [12]. The fabrication process of the silicon (Si) cantilevers includes two deep reactive-ion etching (DRIE) steps in serial order to define cantilever outlines at the front and substrates open at the back. This is followed by removal of the oxide layer, which is used as an etch stop layer for the DRIE step. The processed

wafer is cleaved into several pieces so different thicknesses of VACNT films through exposure are grown on samples. Vertically aligned SWCNT films are grown by using an alcohol catalytic chemical vapor deposition process, and detailed in [25]. A 50 nm SiO₂ layer is first grown on the substrates and the catalyst films (10 nm-thick Al and 0.2 nm-thick Co) are deposited. SWCNT films are then synthesized using ethanol (1.3 kPa) as the carbon source at 800 °C for different time frames. Analysis of the SWCNTs reveals that the growth provides almost 100% of the SWCNTs with the number density of 10¹² cm⁻² [26, 27]. Vertically aligned MWCNT films are grown using a chemical vapor deposition process, as described in [28–30]. Prior to CVD, Al₂O₃/Fe layers are deposited, and all pre-heater gas lines (He, H₂, and C₂H₄) are flushed for 10 min followed by 10 additional minutes of He to displace trapped air from the system at 750 °C. A flow of He (73 sccm) and H₂ (400 sccm) is then introduced over the target substrate for 5 min. A mixture of He/H₂/C₂H₄ (73/400/200 sccm) is introduced for reference substrates during which the CNT array emerges. This process provides a relatively thick film with the number density of ~10¹⁰ cm⁻².

2.2. Data interpretation of the in-plane modulus

Scanning electron microscope (SEM) images reveal that the actual arrangements are substantially complicated by showing many crossings and connections between CNTs as shown in figure 1(b). We assume that a VACNT film behaves as a solid and continuous material structure where all the tube crossings are linked. Based on this continuum assumption, a resonator measurement technique is used to extract the effective in-plane moduli of CNT films. The resonator technique infers the mechanical properties of the tested film, such as effective in-plane modulus. An LDV characterizes the mechanical properties of the nanostructured film by capturing the resonant frequency of the cantilevers before and after the film growth, and after the etching.

Using a Si-CNT composite beam, the effective modulus of CNT film can be extracted as [12].

$$E_{\text{CNT}} = \frac{E_{\text{Si}}}{I_{\text{CNT}}} \left(\left(1 + \frac{\rho_{\text{CNT}} A_{\text{CNT}}}{\rho_{\text{Si}} A_{\text{Si}}} \right) \cdot (1 + \Delta)^2 I_{\text{Si}_0} - I_{\text{Si}} \right). \quad (1)$$

We use the effective $\overline{EI}$ and $\overline{\rho A}$, where E , I , ρ , and A , are respectively the modulus, the second moment of area, density, and cross-sectional area of the beam [12, 31, 32]. The subscripts, Si₀, Si, and CNT denote the silicon layer of a silicon-only cantilever, the silicon, and the VACNT layer of a Si-CNT composite cantilever, respectively, and Δ is the ratio of the resonant frequency shift with the Si-CNT beam to the original resonant frequency of the silicon beam. We use the transformed section method that converts the cross-section of a composite beam into an equivalent cross-section of an imaginary beam, which is then modeled as one material. The distances y to the centroid, values of I_{Si_0} , I_{Si} , I_{CNT} and Δ from the measurement are used as input parameters to equation (1). Because of the modulus weighted centroid calculation, we iterate to find the correct E_{CNT} and I_{CNT} using Matlab code. The density (ρ_{CNT}), another input parameter to equation (1), is estimated based on the thickness

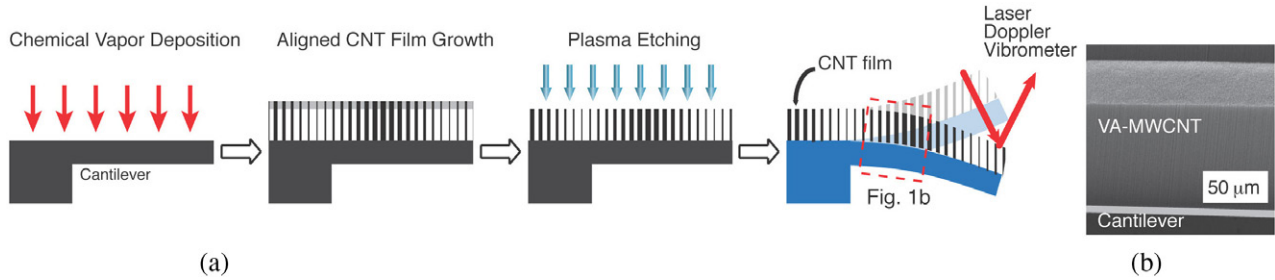


Figure 1. (a) Schematic of the mechanical characterization process of in-plane modulus using a Si-CNT composite beam before and after the etching. Beam dimensions are scaled to achieve a range of resonant frequencies. VACNT film thicknesses are also varied to characterize the mechanical properties of different layer thicknesses. The fabrication process of the microcantilevers is detailed elsewhere [12]. (b) SEM image of a Si-MWCNT composite beam.

and mass measurement of CNT layer using a microbalance (SE2 Ultra Micro Balance, Sartorius) with a $0.1 \mu\text{g}$ resolution and cross-sectional SEM. The details of the measurement process are explained elsewhere [12]. We validate this methodology with a finite element method (FEM) model, by using a film with same modulus and thickness to compare the resonant frequency shift [13]. A good agreement between the measurements and simulation has been observed for thin films. However, the modulus is particularly underestimated for thick films, which introduces a modification factor using FEM models from a previous study. The resulting modulus increases by about 20%. This might be because of transverse shear strain or damping effects, which are usually more significant for thick films.

3. Results and discussion

We recently reported that nanotube characteristics such as alignment, density, and height impact the film's mechanical properties, including elastic modulus [19]. The nonhomogeneous regions of VACNT films exist because of their growth process which results in a denser and entangled crust layer above layers which can decrease in alignment toward the substrate [33]. Bedewy *et al* [18, 34] identified variations in morphology by investigating the growth height and density over time and correlating observed morphology changes to the growth process dynamics including catalyst diffusion and coarsening, and CNT population dynamics such as crowding, self-organization, and termination. These studies have revealed four different stages of the growth process. The first stage is the interweaving of a thin layer of entangled and randomly oriented nanotubes, which forms a crust on the top of the VACNT film. The crust extent varies for a given process depending on growth conditions. The crust is observed to be $1 \mu\text{m}$ thick for the SWCNTs and $0.4 \mu\text{m}$ thick for the MWCNTs in this work. The first stage begins the self-organization that is manifested in the second stage morphology. The second stage is the vertically aligned growth beneath the top crust. As a next stage, the CNTs may have density decay region in the bottom. The CNTs grow at the same speed as the previous stage, but the mass density per unit area can slowly decrease. This results in less aligned and less dense morphology in the bottom region of the film. The final stage is the termination step of the nanotube growth. Note that the third and fourth stages are dependent on

the film height, i.e. if film height is controlled by quenching the growth process (removing carbon feedstock and/or temperature) to achieve a desired height that is less than the termination height allowed by catalyst evolution (typically in the range of 1 mm for MWCNT arrays), then the third and fourth stages are less important. Detailed micrographs of a crust with a larger magnification are shown in figures 2(a) and (c). The mechanical moduli of $\sim 10 \mu\text{m}$ -thick SWCNT films and $\sim 90 \mu\text{m}$ -thick MWCNT films are shown in figures 3(a) and (b). The SWCNT films have an in-plane modulus ranging from 40 to 80 MPa. The MWCNT films have low modulus around 1 MPa. There is no thickness dependency since the crust ($0.5\text{--}1 \mu\text{m}$ -thick in this work) is $<0.5\%$ of the total thickness for the MWCNT films.

Past work shows a clear trend of decreasing in-plane modulus with increases in film thickness ranging from $0.5\text{--}200 \mu\text{m}$ [12, 13]. This is attributed to the presence of a thin and entangled crust layer as described above. The crust layer is measured to be denser than the middle layer. The higher density in combination with the horizontal orientation of the tubes suggests that the crust has higher in-plane stiffness than the middle layer [19]. In many cases, CNT films are metallized, which then allows a metal layer to form a solder bond between a CNT film and target substrates [35]. The metallization is only about 200 nm thick. The solder penetrates the crust layer of the CNT film, which might decrease the crust effect on the mechanical properties of these films when used as TIMs. The modulus measurements are performed before and after the surface etching of the VACNT films to isolate and distinguish the effect of the crust on the properties of the film.

To understand the role of the crust layer, and to characterize films without the crust layer, we developed an etching technique capable of removing the crust layer. An O_2 plasma etch process is used to remove the crust and top layer of the VACNT films resulting in a reduction of the VACNT film thicknesses [36]. We have used RF power (45 W) or O_2 flow rate (80 sccm), resulting in an etching rate of $1\text{--}2 \mu\text{m min}^{-1}$. Figures 2 and 4 show SEM micrographs of SWCNTs and MWCNTs before and after O_2 plasma etching. In figures 2(a) and (c), the tips of the CNTs are entangled, forming a wavy crust layer. Figure 4 shows that the top crust layer of the CNTs is removed by the O_2 plasma etching. The transformed morphology is clearly illustrated in a close-up view in figures 4(a) and (b). Some tips of the CNTs attach and fix themselves to each other, forming needle shapes instead of displaying entanglements.

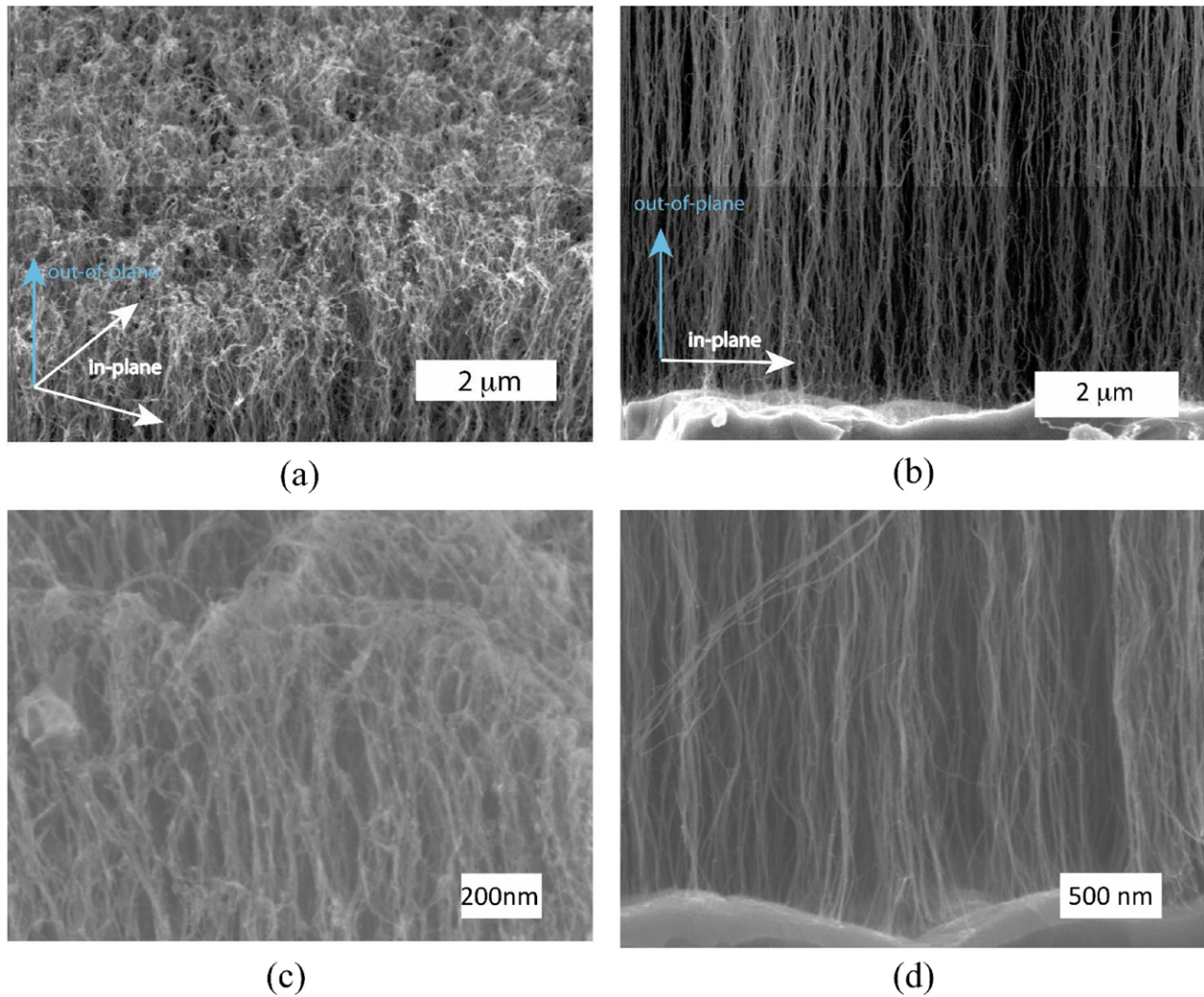


Figure 2. SEM images of MWCNT and SWCNT films. (a) SEM image of a crust layer and (b) middle layer of a MWCNT film. (c) SEM image of a crust layer and (d) middle layer of a SWCNT film. SEM images (a), (c) show the top portion of CNTs indicate more entanglements and connections between CNTs. SEM images (b), (d) show the middle and bottom portion of CNTs are vertically aligned.

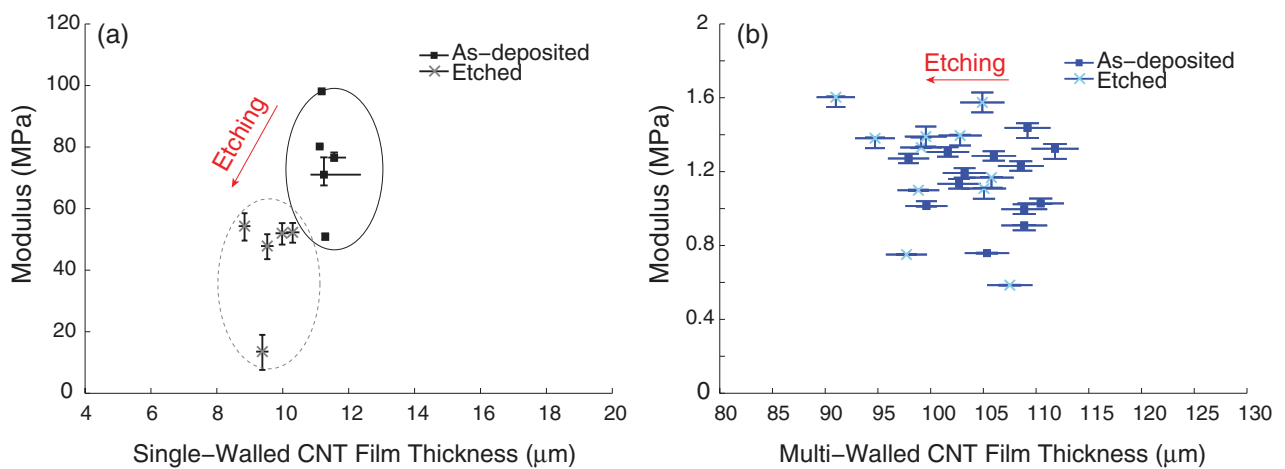


Figure 3. Effective modulus of (a) SWCNT films and (b) MWCNT films after the surface etching. Solid squares and crosses represent the moduli before and after the etching, respectively. The thickness nonuniformities are indicated by the horizontal error bars. The nonuniformity effects on the modulus are represented by the vertical error bars. Although the thick MWCNT films exhibit relatively large thickness nonuniformities, the effects on the modulus are reasonably small.

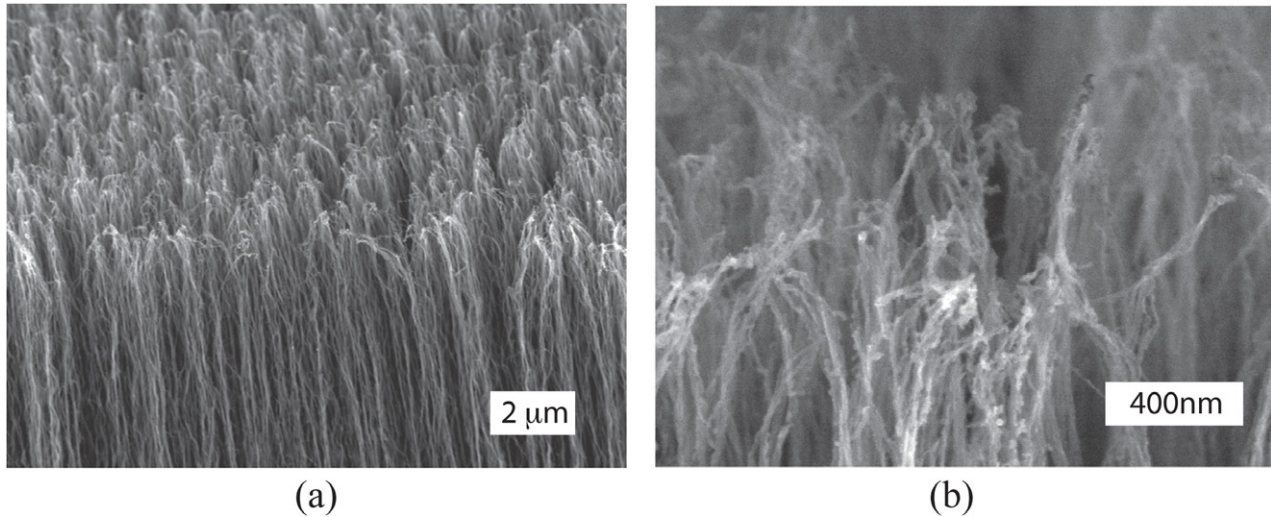


Figure 4. SEM images of MWCNT and SWCNT films. (a) MWCNTs and (b) SWCNTs after the surface etching. The surface etching removes the entanglements and connections between CNTs.

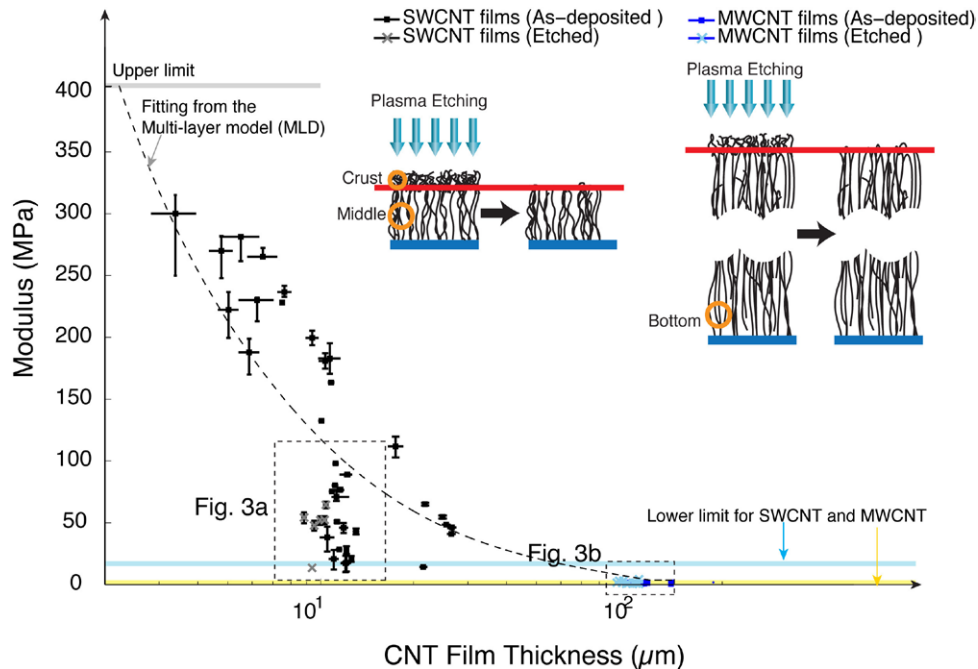


Figure 5. Modulus of SWCNT and MWCNT films [31] before and after the surface etching. Data sets show that the modulus decreases as the film thickness increases. The plot indicates the fitting line from the multi-layer model (MLD) [12] using the upper and lower limit to represent the crust and middle layer. The plot includes data on samples from a previous study that were not etched. The etched samples are boxed. (Inset) Schematics of vertically aligned SWCNT and MWCNT films before and after the etching. The SWCNT films have a crust and middle layer, and the MWCNT ($>90 \mu\text{m}$) films have a crust, middle, and bottom layer.

Additionally, the CNTs appear more vertically oriented after the etching than they were before the etching. The enhancement in vertical orientation may be associated with the effect of a strong vertical electric field during the plasma etch process, which may induce vertical alignment of the CNTs [37]. Thus, the vertical alignment can contribute to a lower in-plane mechanical modulus. In addition, damage or nonuniformity after the surface etching is another potential factor affecting the overall mechanical response of the film. Therefore, this factor should be carefully investigated in future work.

The SWCNT films received a 1 min surface etching. This etching reduces the film thickness from 11–14 μm to 9–12

μm and removes the crust layer with a height of $\sim 1 \mu\text{m}$. Since the portion of the crust is relatively large (7–11% of the film thickness), the crust can significantly affect the overall density and mechanical properties of the film. In figure 3(a), the moduli before the etching are shown with black squares, and the moduli after the etching are represented with gray crosses. Figure 5 shows that the modulus of as-grown films increases as the film thickness decreases due to the impact of the crust on the modulus. Figure 3(a) shows that the etched films have a lower modulus after the plasma etch. This reduction of modulus for thinned films is the opposite of the previous trend for the dependence of modulus on film thickness because of the

removal of the crust layer in this experiment. The remaining film comprises the middle and base layers, which have a lower density and in-plane modulus than the crust. Therefore, the density and moduli of the entire films without the top crust layer will have decreased; the moduli of the etched films are smaller than the grown films with same heights.

The MWCNT films have lower density, alignment, and more significant density decay in the bottom part than the SWCNT films. These MWCNT films received a 5 min surface etching. This etching removes the top crust and reduces the film thickness from 95–115 μm to 90–105 μm . In figure 3(b), the moduli before and after etching of the MWCNT films are represented with blue squares and crosses, respectively. There is no significant difference in modulus between the etched and as-grown films. For thick films ($>90\ \mu\text{m}$), the crust of ($\sim 0.4\ \mu\text{m}$) occupies a smaller portion of the entire film ($<0.5\%$); the crust effect on the overall density and extracted modulus is relatively small. In addition to the crust effect, the low modulus of MWCNT films may be attributed to the bottom region of the thick films resulting from the density decay stage [18, 34]. This bottom region of sparse or unaligned nanotubes might reduce the mechanical modulus of an entire film.

4. Concluding remarks

In this paper, the microfabricated resonator technique is used to measure the in-plane moduli of $\sim 10\ \mu\text{m}$ -thick vertically aligned SWCNT films and $\sim 90\ \mu\text{m}$ -thick vertically aligned MWCNT films to be in the range of 80 MPa and 1 MPa, respectively. The mechanical data sets show the strong dependence of the SWCNT film modulus on film thickness due to morphology variations (crust, middle, and bottom regions) through the film thickness while the morphological effect is not obvious for the MWCNT films in the thickness ranges considered ($\sim 90\ \mu\text{m}$ thick films). Removal of the unaligned crust layer reduces the in-plane modulus, consistent with micromechanics of aligned and unaligned fibrous structures. To use these VACNTs as TIMs, the crust region and bottom region of the VACNT film will be embedded in thin metal layers for use in a solder bonding process. Therefore, it is particularly important to isolate and understand the effect of the crust on the metal deposition and the resulting mechanical properties of VACNT films. The surface etching removes the crust of entangled nanotubes from the VACNT film and changes the film thickness, as revealed in SEM images. The moduli of the films before and after etching are measured using SWCNT and MWCNT films [31], and the images of the SWCNT and MWCNT films before and after the etching are investigated. Because of the large effect of the crust on the measured modulus values for SWCNT films, the etching step improves the mechanical compliance of the SWCNT films ($\sim 10\ \mu\text{m}$), which is suitable for use as an interface material. Regardless of the presence of the crust, the range of the low mechanical moduli of MWCNT films is promising for a variety of applications including thermal interfaces. Future work will address potential changes in morphology associated with surface etching. The new morphology may induce differences in

nonuniformity and density, which can affect the mechanical behaviors of the entire films. To account for those factors, the etched films should be characterized using other techniques, such as Raman spectroscopy or x-ray absorption. Our plans for future work also include studies of bonding materials and integration of the CNT TIM between two surfaces that show different thermal expansion coefficients.

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