FABRICATION AND MECHANICAL PROPERTIES OF CARBON NANOTUBE COMPOSITE MICROTRUSSES

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Keywords: Carbon Nanotubes, Microtruss, Atomic Layer Deposition, Stiffness, Damping, Toughness

1. Introduction

Metallic foams and periodic cellular structures have been investigated widely for energy absorption, thermal management, vibration damping, and structural load support applications [1, 2]. Periodic microtruss geometries, which comprise angled solid members that connect at node points, have been of interest because careful control of their geometry and periodicity [3-5] enables high stiffness, strength, and energy absorption at relatively low density. These properties compare favorably to those of metallic foams due to more efficient placement of constituent material [6]. In addition, the fabrication of such microtrusses may have further use in hierarchical micro/nanostructures to achieve simultaneously high stiffness and damping [7].

Microtrusses have been fabricated by methods including lithography of self-propagating photopolymer waveguides [8], rapid prototyping of acrylonitrile-butadiene-styrene (ABS) patterns followed by investment casting of beryllium-copper alloy [9], weaving of stainless steel wires [10], and selective laser melting of metal powders [11]. Recently, a template fabricated by self-propagating photopolymer waveguide prototyping was coated by electroless nickel plating to create ultralight metallic microlattices with density less than 0.9 milligram per cubic centimeter [12]. However, in general methods of fabricating the slanted micro-scale members are serial rather than parallel, and require multiple steps such as sacrificial conversion of a polymer to a metal to give robust mechanical properties.

We demonstrate a novel method of fabricating microtrusses by using patterned carbon nanotube (CNT) “forest” growth as a template. Due to the high stiffness at low bulk density [13, 14] of CNT forests, and compatibility with conformal coating by Atomic Layer Deposition (ALD), this approach enables utilization of aligned CNTs in microtrusses with tunable mechanical properties and deformation behaviors. We show that tuning of ceramic coating from 20 to 1000 cycles of ALD results in tuning of the CNT based composite microtruss modulus from 10-2150 MPa, which is comparable to tunability previously achieved for Ni-based microlattices (710 KPa - 580 MPa) [15] and photopolymer microlattices (96 – 182 MPa) [8]. We also demonstrate that the deformation behaviors change drastically depending on the coating thicknesses and at coating thickness corresponding to 100 cycles of ALD, the CNT microtrusses exhibit extremely high strain recovery.

2. Fabrication

2.1 Microtruss Design

CNT microstructures were fabricated in the microtruss geometry, where a center member and 4 adjacent bent members come together at an apex to create a node. The bent CNT microstructures were
fabricated by stress mediated growth rate modulation. Topology optimization was performed where the angles of the laterally deflected CNT members were tuned by varying the overlap of growth rate modulation layer and the CNT catalyst layer to achieve the desired geometry. Then the microtrusses were reinforced with Al$_2$O$_3$ coating to enhance their stiffness and strength.

2.2 CNT Microtruss Fabrication

In order to create the 'microtruss' geometry with CNT microstructures, a scheme of creating curved CNT microstructures was needed. For this, a TiN layer underneath the CNT growth catalyst was used as a growth rate modulator causing the desired CNT micropillars to bend during growth and form the truss members.

Two lithography steps were needed as the TiN underlayer was patterned before the CNT catalyst layer. First, the desired TiN layer pattern was defined on a silicon wafer by photolithography using a photoresist (SPR 220-3.0). TiN was sputtered, and lift off was performed on the entire wafer. The lift off procedure consisted of ultrasonication in acetone for 8 minutes twice then rinsing with isopropanol, then blow-drying with nitrogen. Then the second lithography step was performed to pattern the desired CNT catalyst shapes on the same wafer. A catalyst supporting layer (10 nm of Al$_2$O$_3$) and the catalyst (1 nm of Fe) were sputtered onto the patterned wafer. Once these films were deposited, the wafer was diced to appropriate sizes and lift off was performed again.

Once the silicon wafer pieces were prepared, the CNTs were grown by a thermal Chemical Vapor Deposition (CVD) process in a quartz tube furnace. The wafer pieces were loaded into the quartz tube and the end caps were tightened to seal the system, and then it was flushed with 1000sccm of He for 5 minutes. Then, under 400/100sccm of He/H$_2$ flow, the temperature was ramped to 775°C in 10 minutes, then was held for another 10 minutes to anneal the catalyst. Then, 100sccm of C$_2$H$_4$ was added, which starts the growth of CNTs. The C$_2$H$_4$ flow was maintained for the duration necessary to achieve the desired height; the CNT growth rate was approximately 50 μm/minute under these conditions.

Fig. 1. a) Growth rate modulation leading to curved as-grown CNT microstructures b) Microtruss topology tuning by varying the overlap of catalyst and growth retardant layer c) An SEM image of a large array of CNT microtrusses with selected topology d) Cylindrical CNT microstructures with various diameters to compare against CNT microtrusses
The effect of varying the overlap between CNT catalyst layer and TiN growth rate modulation layer is shown in Fig. 1a. The truss angle therefore was controlled by varying the portion of Fe/Al₂O₃ on SiO₂ and TiN. A larger overlap results in steeper bending angle (measured from the vertical axis) and smaller radius of curvature, as it leads to a bigger portion of CNT microstructure growing slowly. By this method, a large array of CNT microstructures having desired topology was grown on a silicon wafer substrate (Fig. 1b,c) by thermal CVD.

2.3 Mechanical Reinforcement

In order to tune the mechanical properties of the CNT microstructures, reinforcement with Al₂O₃ was performed. Atomic Layer Deposition (ALD) is used to create a conformal coating of Al₂O₃ [16] on the individual CNTs within the microstructures, and to fill the forest with this coating. Each cycle of ALD process deposits approximately 0.1 nm of Al₂O₃ and coating thicknesses from 2-100 nm have been used in this study as shown in Fig. 2 a), b) and c). The coated microstructures were cleaved to assess the depth of penetration of the coating. As shown in Fig. 2 d), the depth of penetration of the coating is approximately 5 μm. To benchmark the properties of the reinforced microtrusses, cylindrical CNT microstructures were also prepared.

3. CNT Microtruss Properties

3.1 Measurement

The CNT micropillars and microtrusses were characterized by a nanoindenter (MTS Nanoindenter XP) using a 100μm diameter flat sapphire tip. The indentation was performed at 150nm/s. In situ SEM compression was performed using a custom-built micromechanical test frame within an FEI Quanta ESEM. A 125μm diameter sapphire flat punch was used for in situ SEM compression.

3.2 Deformation Behavior and Recovery

In situ SEM compression was performed to capture the deformation behavior of CNT microtrusses. Depending on the thickness of the coating, the deformation behavior of reinforced structures changes drastically. This because individual CNTs in a microstructure are tangled and tortuous, and reinforcement by Al₂O₃ coating serves to cement the joints where the individual CNTs meet; moreover, the coating reinforces the spanning regions of the CNTs by creating core-shell composite beams. Also, CNT microstructures are effectively foam-like materials, and this limits the ability of ALD
precursors to penetrate the entire structure and conformally coat the CNTs in the center of the structures. These characteristics lead to the reinforced CNT microstructures to exhibit shell-like deformation behavior.

First, we consider the deformation of the straight cylindrical test structures. With 2 nm (20 cycles) of ALD Al₂O₃, the microstructure deforms at the base by developing accordion-like wrinkles and recovers very little (Fig. 3). This is consistent with findings by Cao et al. [17] when compressing as grown CNT forests. This shows that thin ALD Al₂O₃ coatings do not modify the deformation behavior of CNT microstructures. Once the microstructure buckles and the load is removed, some plastic deformation is evident from both the load-displacement curve and the in situ SEM images.

With 10 nm Al₂O₃, the microstructure undergoes large elastic deformation resembling buckling of a cylindrical shell under axial compression, and recovers almost fully (Fig. 4). Global strains up to 50% have been shown to recover almost fully. At this coating thickness, the spaces between individual CNTs are not yet fully filled (nominally 100 nm distance between individual CNTs) but the outer shell is considerably reinforced, evidenced by the increase in stiffness. Once the local buckling occurs in the shell, the CNTs are strained, but do not snap, and the elastic energy stored in the CNTs is the driving force behind the recovery. Because the CNTs are not embedded in a rigid matrix and are arranged in a very tortuous manner, they will be able to slide past each other and straighten out according to the applied load, without failing catastrophically.

The large hysteresis and recovery observed at this coating thickness can possibly be utilized in energy dissipation applications. Rotation at nodes has been attributed to large strain recoverability in hollow metallic microlattices [15] rather than the deformation of the struts themselves. In the case of CNT/Al₂O₃ microtrusses, the truss members themselves undergo extremely large deformation and full recovery.

With 100 nm Al₂O₃, the microstructures undergo brittle fracture and fail catastrophically (Fig. 5). At this coating thickness, the spaces between CNTs in the outer shell are almost completely filled, and the CNTs are cemented in their spatial positions relative to each other. This will dramatically increase the stiffness as the outer shell is now continuous and can support much more load. However, crevices between bundles of CNTs coated with ceramic still exist (as shown in Fig. 2d), and will serve as stress concentration points as the compressive load is applied. As the applied load increases, cracks develop between CNT bundles and the entire
structure barrels outward with fracture propagating parallel to the CNTs. As the load is further increased and the compressive load causes local buckling in each 'plank' of the barrel, the CNTs are not able to rearrange and bend or straighten out, therefore the individual 'plank' snaps at the weakest point.

3.3 Stiffness and Energy Absorption

Example load-displacement curves are shown in Fig. 6 for microstructures and Fig. 7 for microtrusses. The microtruss stiffness was calculated by taking the slope of the unloading region of the compressive load-displacement curve, and normalizing by the total cross sectional area of the constituent members.
Fig. 6. Load-displacement curves of cylindrical CNT microstructures with various numbers of ALD Al₂O₃ coating cycles a) 20, b) 100, c) 1000. Insets show maximum compression in \textit{in situ} SEM compression testing.

Fig. 7. Load-displacement curves of CNT microtrusses with various Al₂O₃ thicknesses: a) 2nm, b) 10nm, c) 100nm. Insets show maximum compression in \textit{in situ} SEM compression testing.
The stiffnesses of the CNT microstructures and microtrusses with various coating thicknesses are plotted in Fig 8. Because only the center post is parallel to the direction of compression, some degradation of stiffness is expected when compared to the vertically straight microstructures. Also, as the contact surface between the indenter tip and the microtruss may not be perfectly flat, further lowering of the stiffness is expected.

Due to the constituent CNT/Al$_2$O$_3$ members having large tunability of stiffness, the microtrusses made from these members also show a wide range of stiffness depending on the coating thicknesses only. Studies have shown that strut dimensions, density, and angle [8, 15] can be varied to tune the stiffness of a given microlattice. Even without such geometric tuning, the range of stiffness that we have achieved (10-2150MPa) is comparable to those shown in literature (710Pa-580MPa for Ni-based microlattices [15], 96-182MPa for photopolymer microlattices [8]).

Cyclic loading and unloading of these microtrusses were performed to characterize the energy absorption capacity. The microtruss with 10nm coating thickness has high hysteresis due to its high recovery. The specific damping capacity (SDC), $\psi$, defined as the ratio of dissipated energy per cycle to the stored energy, for these microtrusses is 0.757.

4. Conclusions

We demonstrate that the stiffness of CNT microtrusses coated with ceramic can be tuned over a wide range comparable to those of previously reported metal/photopolymer based microlattices. The range of stiffness achieved for the CNT microtrusses is solely due to the mechanical reinforcement with ceramic coating. Further tuning of the microtruss stiffness can be expected if the truss member angles, dimensions and densities are also controlled. Moreover, we have shown that different ceramic coating thicknesses influence the deformation behavior of the struts themselves, from accordion-like buckles to elastic shell buckling to brittle fracture. In the future, addition, engineering of coatings and filling the voids with high loss polymer could achieve simultaneously high stiffness and damping in a laminated configuration.

5. Acknowledgements

This work was supported by the Defense Advanced Research Projects Agency (HR0011-10-C-0192). Support from DARPA was received under Agreement to NextGen Aeronautics, and any opinions, findings, and conclusions or recommendations expressed in this material do not necessarily reflect the views of NextGen Aeronautics and/or DARPA.

References


