

Tailoring the Mechanical Properties of High-Aspect-Ratio Carbon Nanotube Arrays using a-SiC Coatings*

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Abstract

The porous nature of carbon nanotube (CNT) arrays allows for the unique opportunity to tailor their mechanical response by the infiltration and deposition of nano-scale conformal coatings. Here, we fabricate novel photo-lithographically defined CNT pillars that are conformally coated with amorphous silicon carbide (a-SiC) to strengthen the interlocking of individual CNTs at junctions using low pressure chemical vapour deposition (LPCVD). We further quantify the mechanical response by performing flat-punch nanoindentation measurements on coated CNT pillars with various high-aspect-ratios. We discovered new mechanical failure modes of coated CNT pillars, such as "bamboo" and brittle-like composite rupture as coating thickness increases. Furthermore, a significant increase in strength and modulus is achieved. For CNT pillars with high aspect ratio (1:10) and coating thickness of 21.4 nm, the compressive strength increases by an order of magnitude of 3, towards 1.8 GPa (from below 1 MPa for uncoated CNT pillars) and the elastic modulus increases towards 125 GPa. These results show that our coated CNT pillars, which can serve as vertical interconnects and 3D super-capacitors, can be transformed into robust high-aspect-ratio 3D-micro architectures with semiconductor device compatible processes.

12 Keywords: carbon nanotubes, nanoindentation, pillar compression, coating, failure

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13 I. INTRODUCTION

14 Vertically aligned carbon nanotube (CNT) arrays or forests in photo-lithographically de-
15 fined patterns have been recognized as a promising structural material for the fabrication of
16 high-aspect-ratio, three-dimensional (3D) micro- and nano-architectures [1–5]. The excep-
17 tional properties of CNTs and related materials have triggered tremendous efforts not only to
18 study their intrinsic properties but also to explore their applications in a large variety of fields
19 [6–13]. These high-aspect-ratio 3D structures play an important role in the advancement of
20 vertical interconnect technology [14–17], flexible batteries [3], stamps for micro/nanoimprint
21 lithography [2, 18–21], compliant thermal interface materials for low inter-facial resistances
22 [22–25], 3D super-capacitors [26, 27] and nano/micro-electromechanical systems (NEMS)
23 and (MEMS) [1, 28–30].

24 The CNT arrays that we refer to in this work are composed of nominally vertical, inter-
25 woven, multi-wall carbon nanotubes [31, 32]. A common procedure for growing high-aspect-
26 ratio CNT arrays is via chemical vapor deposition (CVD) on photo-lithographically defined
27 catalyst areas [5, 9]. One of the limitation of this growth process, is the low packing density
28 of the CNTs inside the array [15, 33]. The interwoven CNTs inside the array are held to-
29 gether by a weak van der Waals interaction, allowing tubes to slide along each other [34, 35].
30 The combination of low packing density and weak inter-tube forces, results in mechanical
31 properties of CNT arrays that are significantly inferior to individual CNTs [6, 35].

32 Consequently, a considerable amount of effort is going into the development of new meth-
33 ods to optimize the full potential of individual CNTs in low density CNT arrays, either by
34 densification or application of conformal coatings. A literature overview of coated nanoscale
35 architectures can be found in [36]. Recent and remarkable examples of conformally coated
36 CNT arrays include *e.g.*, deposition of silicon coatings to create a flexible anode architecture
37 for high-energy-density-batteries [3] and graphene coatings to create superelastic, lightweight
38 and fatigue resistant aerogels [7].

39 Silicon carbide also proves to be an interesting coating material, mainly due to its dia-
40 mond like characteristics [37]. The properties of SiC are especially attractive in applications
41 which require contact, high temperatures, chemical inertness, high robustness, electrical con-
42 ductivity and high resistance to electron beam damage [38–41]. Bulk composites containing
43 SiC-coated CNTs have been produced by chemical vapour infiltration and were tested by

44 bending and a pull-out method. One remarkable result was the protection of CNTs from
45 being oxidized at 1600 °C in air for 1 hour [42]. Investigations have also shown that SiC-
46 coated multi-walled CNTs dispersed in composites increase fracture toughness and hardness
47 [43].

48 The porosity of CNT arrays allows for infiltration and deposition of conformal coatings
49 on individual CNTs inside the array. This results in the possibility to significantly alter the
50 mechanical response of 3D-micro-architectures by changing the deposition thickness.

51 In this paper, we report the fabrication and testing of various high-aspect ratio pil-
52 lars made from carbon nanotube arrays that are modified by thin conformal coatings of
53 amorphous silicon carbide (a-SiC) deposited by low pressure chemical vapour deposition.
54 We perform flat-punch nanoindentation measurements on CNT pillars to characterize the
55 influence of conformal coatings of different thickness on the mechanical response of 3D-
56 micro-architectures. We analyse the structural failure mode by performing scanning electron
57 microscopy investigations after pillar compression. The specimens without coating show lo-
58 calized periodic buckling. Samples with thin coatings show bamboo-like failure while the
59 samples with thick coatings show brittle ceramic failure. Furthermore, a significant increase
60 of 3 orders of magnitude is measured for the compressive strength of pillars with a 21.4 nm
61 thick coating of a-SiC.

62 II. DISCUSSION AND RESULTS

63 Carbon nanotube structures are grown by a common manufacturing process employing
64 CVD on photo-lithographically defined catalyst areas (Supplementary A 1). After growth,
65 the CNT arrays are conformally coated with 5.6 nm, 10.5 nm, 21.4 nm and 52.0 nm thin
66 layers of amorphous silicon carbide (a-SiC) (Supplementary A 2). A matrix of as-grown
67 CNT pillars with circular cross sections is shown in Fig. 1a. The pillars are $(100 \pm 2) \mu\text{m}$
68 tall and have lithographically defined diameters ranging from $(5 \pm 1) \mu\text{m}$ to $(150 \pm 1) \mu\text{m}$.
69 The maximum length to diameter L/D aspect ratio that results in highly vertical pillars
70 is about 10:1. The morphology of the CNT pillars at 50, 100 and 150k magnification is
71 shown in Fig. 1b, here it can be seen that individual CNTs inside the array are nominally
72 vertical and interwoven. The low packing density is mainly caused by the relatively large
73 spacing between catalyst particles which results in large spacing between individual CNTs

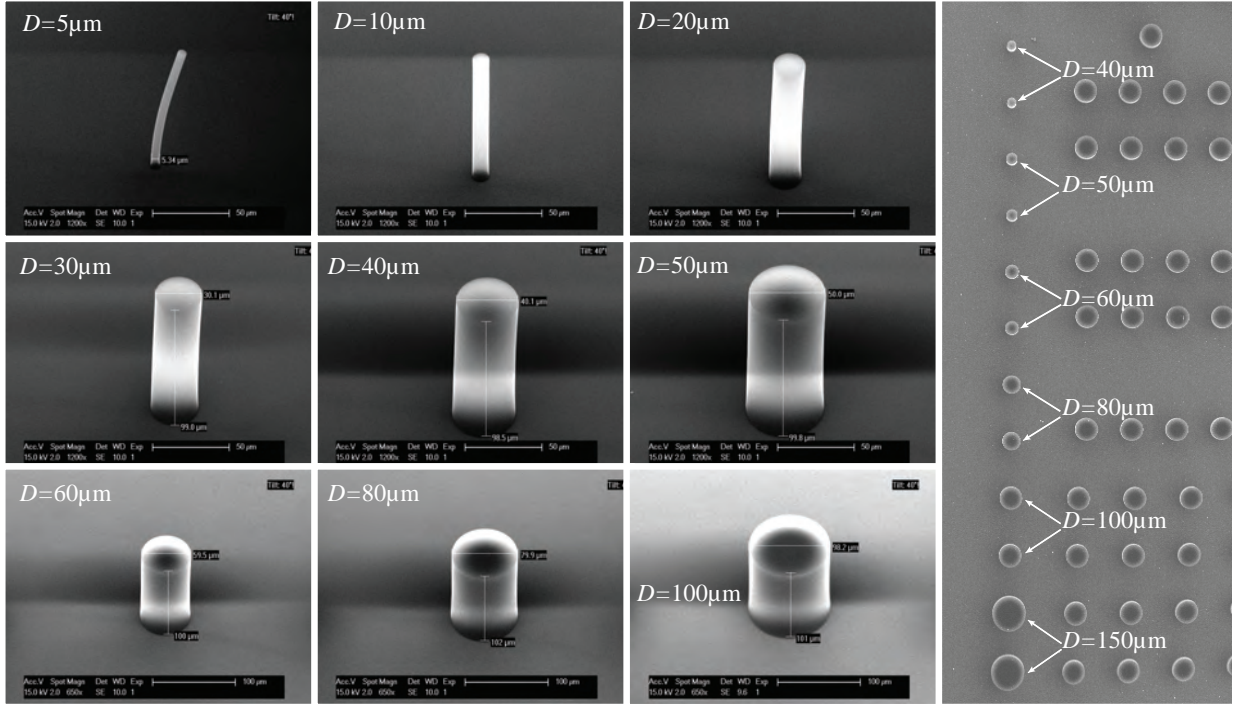
74 [33]. Examination of the CNT arrays at different stages; before and after coating, allows
75 us to verify the coating process. Some single CNT fibres are bundled together into larger
76 fibres due to the van der Waals attraction. The high magnification images in Fig. 1b, show
77 a doubling of the fibre thickness with increasing deposition thickness, following the same
78 trend as the measured film thicknesses of 5.6 nm, 10.5 nm, 21.4 nm and 52.0 nm of a-SiC on
79 bare Si test wafers (Supplementary Fig. S2). The as-grown CNT array density is roughly
80 10^{10} tubes/cm² which is determined from the SEM images of the pillars in Fig. 1b. The
81 samples with a thick coating are still somewhat porous, this shows that precursor gases can
82 still infiltrate the array and deposit a-SiC further inside the bundle.

83 To investigate the coating penetration depth and thickness we cleave several coated mi-
84 cropillars with a Berkovich nanoindentation tip. Afterwards, we use a Verios 460 extreme-
85 high-resolution (XHR) SEM for characterization of the pillar cross-section (Supplemen-
86 tary A 2). The coating thickness reduces with roughly 0.14 nm per 1 μ m surface penetration
87 depth (Fig. S3). Closer inspection reveals that the CNTs, which are sticking out of the
88 broken a-SiC matrix, have an average diameter of about 9 nm (Fig. S4). Furthermore, the
89 high resolution SEM image shows that the coating thickness on the CNTs is in excellent
90 agreement with the film thickness measured by ellipsometry on flat control samples.

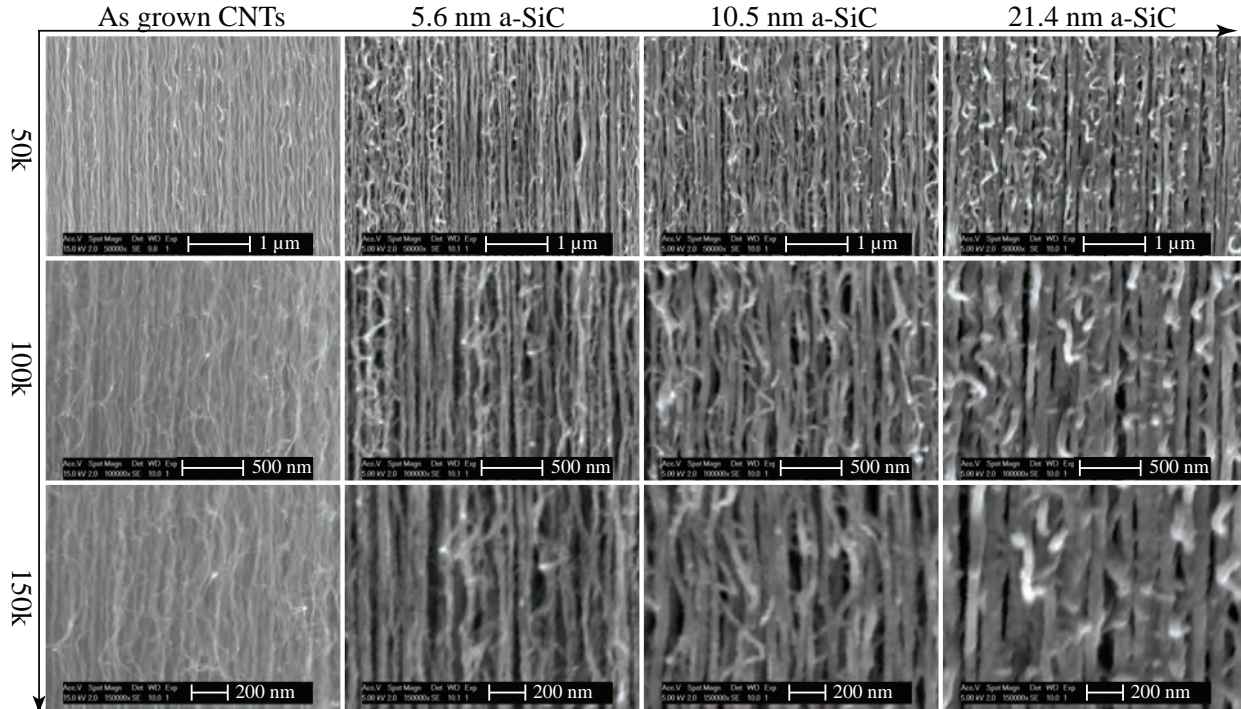
91 A Raman spectrum analysis of the pillars is used to assess the quality of the CNTs
92 before and after a-SiC deposition (Supplementary A 4). The data shows a convolution of
93 the graphite (G) and disordered graphite (D) peaks together with the a-SiC peak into a
94 single wide asymmetric peak near 1475 cm⁻¹ (Supplementary Fig. S5). Deconvolution of
95 the peaks using a least square fitting procedure shows that the intensity ratio I_G/I_D is
96 reduced for thicker films of a-SiC. This indicates that the deposition of a-SiC might have
97 reduced the quality of the CNTs. However, the scattering efficiency of amorphous carbon
98 is relatively high when compared to graphite like carbon. The amorphous carbon would
99 therefore yield a stronger Raman signal, which originates more from surface layers instead
100 of the CNTs.

101 A. Compressive failure of uncoated CNT pillars

102 Uniaxial compression tests of micro- and nano-pillars using flat-punch nanoindentation of-
103 fers a convenient method to effectively study their mechanical behaviour with high accuracy



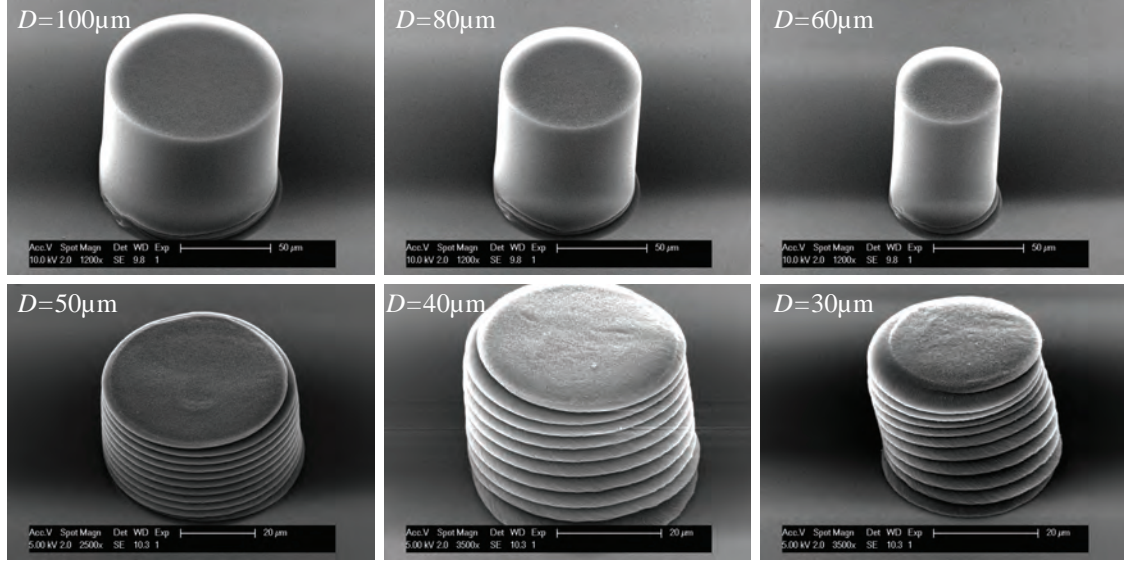
(a)



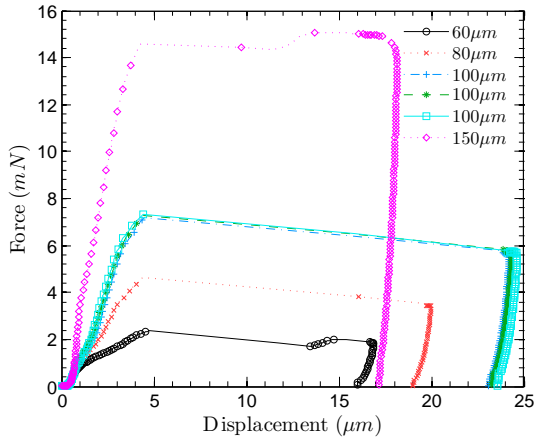
(b)

FIG. 1: Scanning electron microscopy images of (a) CNT pillars with varying aspect ratios on the left tilted views, on the right top view. (b) The morphology of the CNT pillar sidewall before and after a-SiC deposition at different magnifications.

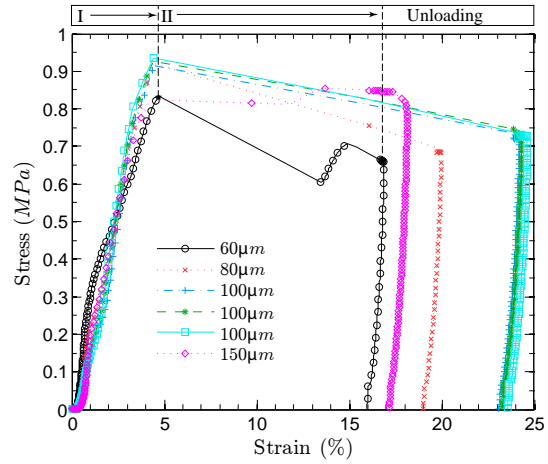
104 and precision [44]. The mechanical response of our CNT pillars under uniaxial compression
105 is characterized using nanoindentation with a custom-made flat-punch diamond indentation
106 tip (Supplementary A 5). Scanning electron microscopy images of uncoated CNT pillars
107 after compression reveal that the pillar failure mode is a type of localized periodic buck-
108 ling which initiates at the base and propagates upwards throughout the entire bundle for
109 increased compression depth, see Fig. 2a. The top three pillars with 100, 80 and 60 μm diam-
110 eters were compressed 25, 20 and 17 % respectively and show 1 or 2 buckling-wavenumbers.
111 The bottom three pillars with 50, 40 and 30 μm diameters were compressed 80% and show
112 wavenumbers in the range of 9 to 11. These typical buckling characteristics appear to be
113 unique for uncoated CNT arrays. More importantly, the localized periodic buckling events
114 are very reproducible and in excellent agreement with the in-situ CNT array compression
115 observations from *Shelby* and *Maschman et. al.* [5, 9]. Their observations also indicate that
116 buckling events originate at the base of the pillar and the buckling wave-number increases
117 with increasing compression depth of the pillars. The load-displacement and stress-strain re-
118 sponse up until failure of uncoated CNT pillars are shown in Fig. 2b and Fig. 2c respectively.
119 Multiple measurements on different pillars with a 100 μm diameter show a high degree of
120 repeatability. Measurement on a 60 μm diameter pillar show that the stress increases mono-
121 tonically for increasing compression, see regime (I) in Fig. 2c. The maximum stress that
122 can be applied before the pillar collapses is about 0.85 MPa at a critical compressive strain
123 of about 4.8%. When this stress is exceeded the system transitions from a stable regime
124 (I) towards an unstable regime (II) with rapid strain bursts. The large distance between
125 the line markers indicates buckling or structural collapse of the pillar which results in an
126 overshoot of the nano-indentation tip towards the substrate. The displacement control of
127 the nano-indenter-equipment is not fast enough to capture the fast decrease in load when
128 the specimen fails. In the final unloading regime it is shown that the pillars remain perma-
129 nently deformed with little strain recovery $\epsilon_r \leq 2\%$. The volume shrinkage after buckling
130 is therefore about equal to the amount of compression and can be as high as 60% to 80%,
131 see Fig. 2a. Uncoated pillars with diameters below 60 μm proved to be too challenging to
132 measure due to adhesion of the pillars to the indentation tip and are therefore omitted from
133 the results.



(a)



(b)



(c)

FIG. 2: Mechanical response of uncoated CNT pillars. (a) SEM images showing the compressive failure of uncoated CNT pillars of different diameters. The top row was compressed 20 μm , the smaller diameter pillars were compressed 80 μm . (b) The measured load versus displacement and (c) the engineering stress versus strain response.

134 B. Compressive failure of coated CNT pillars

135 An exciting observation can be made from the post compression morphology of pillars
 136 with a 5.6 nm thin conformal coating of a-SiC, see Fig. 3a. We see highly aligned vertical
 137 cracks and barely visible wrinkles on the outer surface which have originated from localized

138 buckling and kinking of the CNT fibres. Furthermore, the failure does not initiate from the
139 base and the distinctive periodic buckling which appeared in uncoated pillars, is no longer
140 observed.

141 The results indicate composite failure in the form of matrix or matrix - CNT interface
142 failure. From a cylindrical perspective, vertical cracks are induced when the circumferential
143 stress at the exterior of the pillar exceeds the composite strength. Circumferential stress is
144 strongly dependent on radius and internal pressure. During compression, the pillar internal
145 pressure might increase due to internal localized periodic buckling events that exert pressure
146 on the surrounding material. As a consequence, a strong diameter dependency is observed
147 in the compressive strength of the coated pillars. The mechanism is then crack propagation
148 inside the matrix parallel to the fibre (CNT) orientation. This leads to gradual crushing
149 and a distinct splitting shape of failed pillars resembling bamboo under uniaxial compressive
150 loads [45, 46].

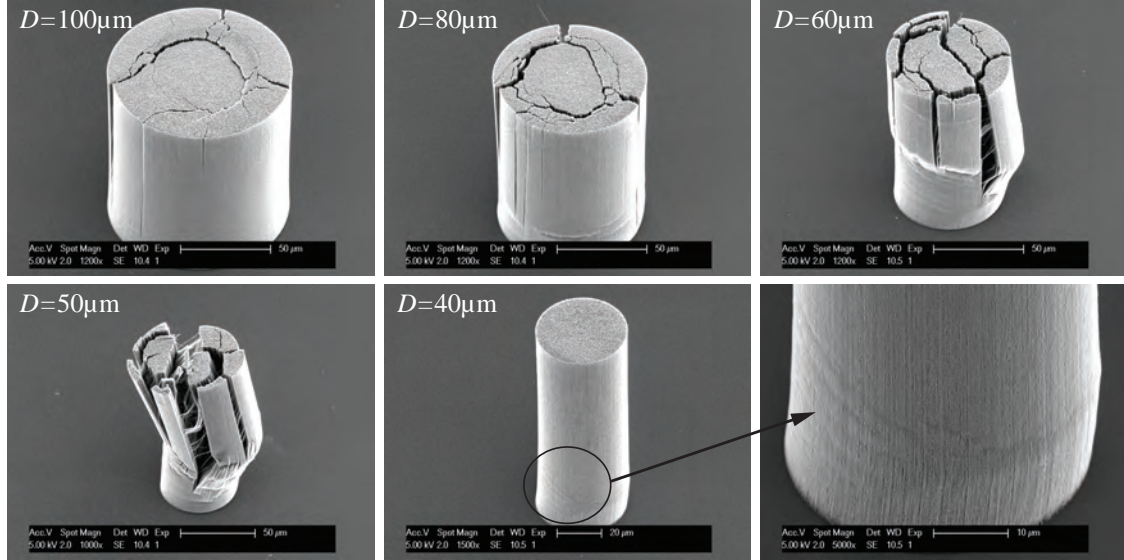
151 When compared to the uncoated CNT pillars, the mechanical behaviour changed from a
152 foam-like material, where the dominant failure mode is localized periodic buckling, towards a
153 bamboo-like failure similar to typical fibre reinforced composites. The accompanying stress
154 versus strain response of the coated pillars see Fig. 3c, show an increase in compressive
155 strength and a strong diameter dependency, where the small 20 μm diameter pillars have
156 higher compressive strengths of about 12 MPa. Three distinct regimes can be identified;
157 regime (I) ($0\% \leq \epsilon \leq 2\%$) elastic deformation, regime (II) ($2\% \leq \epsilon \leq 5\%$) small strain
158 burst propagation, while regime (III) ($\epsilon > 5\%$) shows large strain burst propagation. The
159 regimes (I), (II) and (III) have been illustrated in Fig. 3c for a 100 μm diameter pillar. The
160 compressive strength of the pillars is defined as the maximum stress that can be applied
161 before transition occurs from regime (I) to (II). We think that regime (II) can be attributed
162 to non-periodic local buckling while regime (III) is composite failure and splitting of the
163 bundle.

164 Furthermore, a significant recovery ($\sim 70\%$) of all deformed pillars towards their orig-
165 inal position occurs during unloading even though cracks have appeared. The attraction
166 between CNTs becomes more prominent as they come in closer proximity during compres-
167 sion, which can result in sticking and therefore low recovery of uncoated CNT arrays [47].
168 This suggests that during compression of the samples with 5.6 nm a-SiC coating, the elastic
169 energy stored inside the coated CNTs is enough to overcome the attractive van der Waals

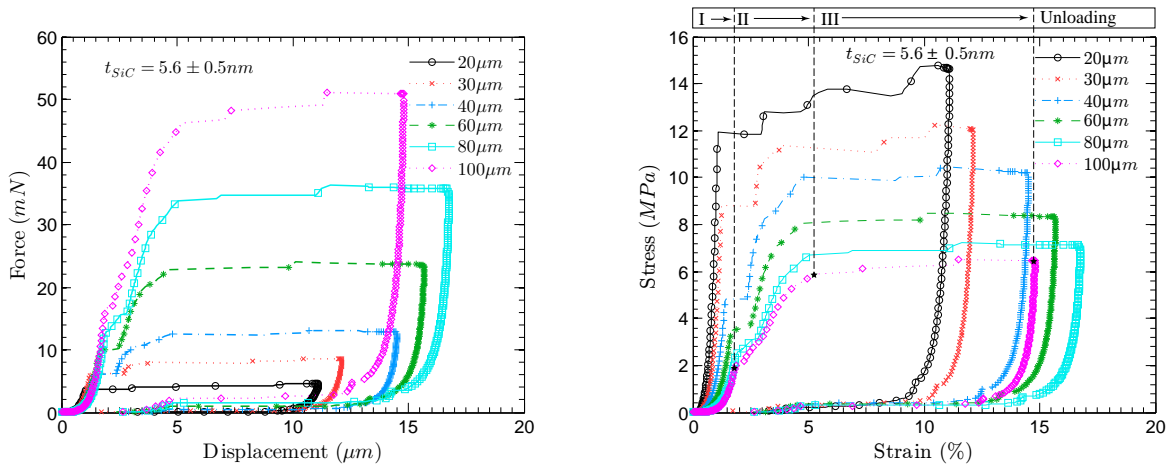
170 force. At the same time the coating is thin enough to allow for a certain degree of flexibility
171 before fracturing. Moreover, the coating interlocks and constrains most of the interwoven
172 CNTs at their junctions. Thus, preventing the tubes from sliding and rotating along each
173 other by replacing the relatively weak van der Waals interaction with a solid cohesive bond
174 and therefore preventing energy dissipation. We hypothesize that these effects combined,
175 attribute to an improved strain recovery of the coated CNT array.

176 Post compression inspection of samples with thicker coatings of 10.5 nm and 21.4 nm
177 of a-SiC, reveal a more destructive failure, see Fig. 4 and Fig. 5 respectively. This can
178 be related to a more dominant brittle failure mode of the a-SiC matrix when the coating
179 thickness is increased. Furthermore, a type of kink banding failure is initiated at the base
180 of the pillar at a similar location as the localized buckling events in uncoated samples. In
181 addition, CNT fibre fracture is observed after compressive failure. The stress strain curves
182 Fig. 6b and Fig. 6d confirm brittle failure due to the almost instantaneous transition from
183 the elastic regime towards structural collapse without yielding, strain bursts or localized
184 buckling events. Finally we tested samples with a coating thickness of 52.0 nm of a-SiC.
185 The pillars were too strong and could not be damaged due to the maximum load limitations
186 of the nanoindentation equipment, see Fig. 6e and Fig. 6f. With the use of a Berkovich
187 tip the pillars were finally destroyed, see Fig. S8. Due to the very strong pillar and violent
188 destruction, the fracture propagated from the pillar into the bulk Si substrate.

190 The compressive strength of CNT pillars with different coating thickness has been exam-
191 ined. Their strength is defined as the maximum stress that can be applied before initiation
192 of strain bursts, buckling or structural collapse occurs. This corresponds with the transition
193 of regime (I) towards regime (II). Fig. 7 displays an overview of the maximum compressive
194 stress of high-aspect ratio coated and uncoated CNT pillars. A high degree of repeatabil-
195 ity is found for measurements on different pillars with a 100 μm diameter, each average is
196 composed of about 12 measurements. For the smaller diameter pillars the average is com-
197 posed of 1 to 4 measurements, since these pillars are fewer in number. The compressive stress
198 increases with thicker coatings and for decreasing pillar diameter. A relatively high compres-
199 sive strength (800 MPa to 1.8 GPa) is achieved for high-aspect ratio pillars ($L/D > 100 : 30$)
200 with 21.4 nm thick coatings of a-SiC. The significant increase in compressive stress is about 3
201 orders of magnitude higher than uncoated pillars. It shows that careful control of nanometre
202 thin conformal coatings of a-SiC can increase the strength of CNT array micro-structures



(a)



(b)

(c)

FIG. 3: Mechanical response of CNT pillars with a 5.6 nm thick a-SiC coating. (a) SEM images showing the compressive failure of coated CNT pillars of different diameters. (b) The measured load versus displacement and (c) the engineering stress versus strain response.

203 by several orders of magnitude.

204 For the uncoated pillars, owing to the low density and waviness of the long and slender
 205 CNTs inside the array, it is expected that they mostly carry bending and torsional forces
 206 instead of normal forces. This draws a strong resemblance with open-cell foams [48, 49].
 207 When a conformal coating of 21.4 nm is applied to the CNTs, the porosity of the array is re-

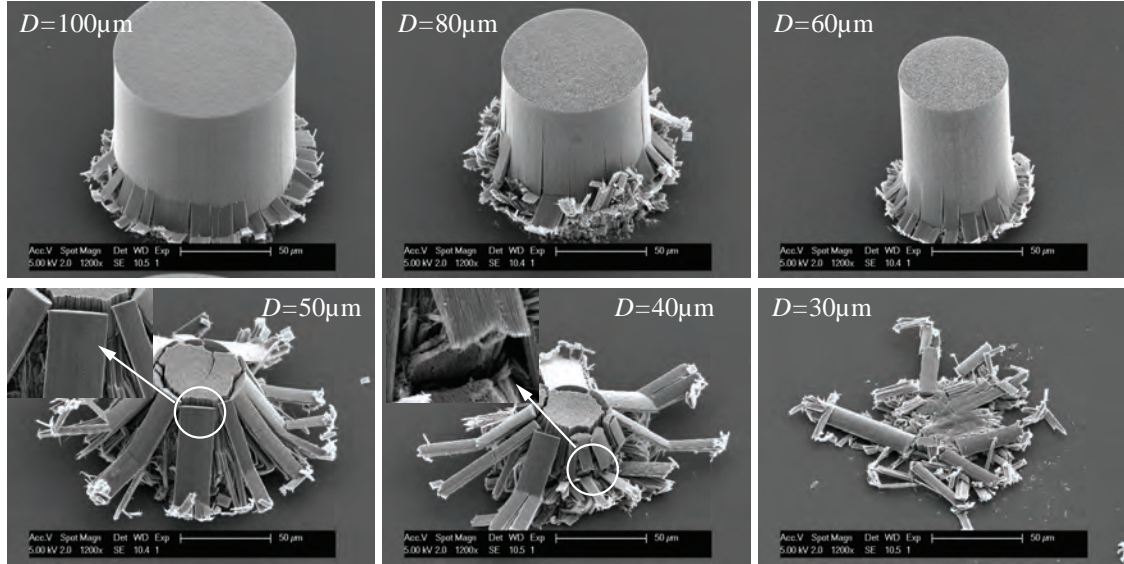


FIG. 4: Compressive failure of CNT pillars coated with 10.5 *nm* a-SiC.

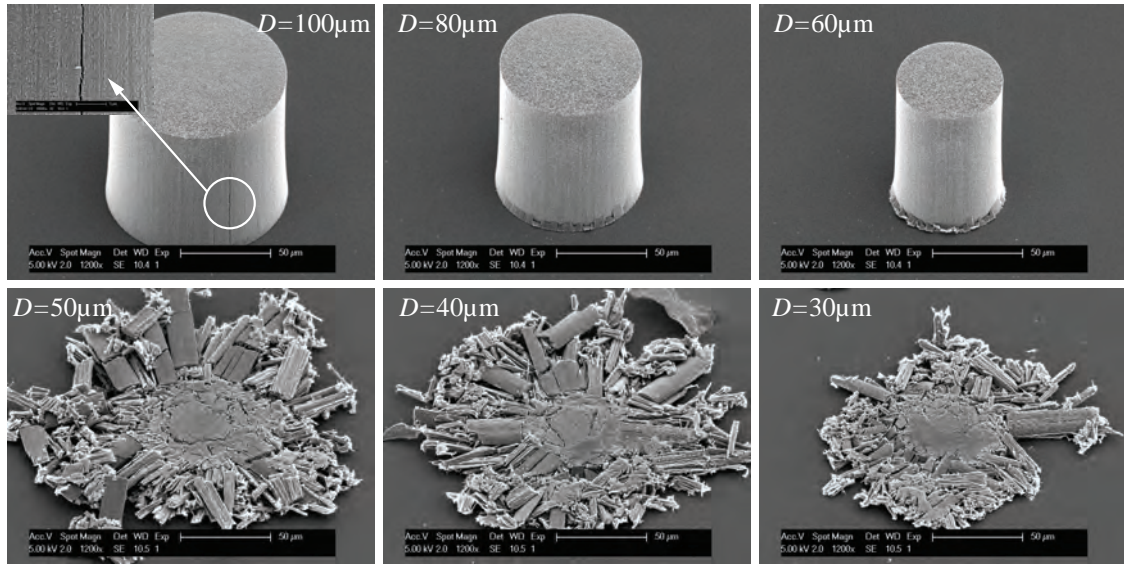
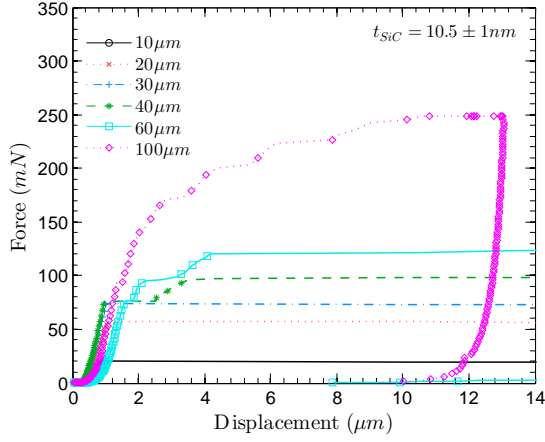
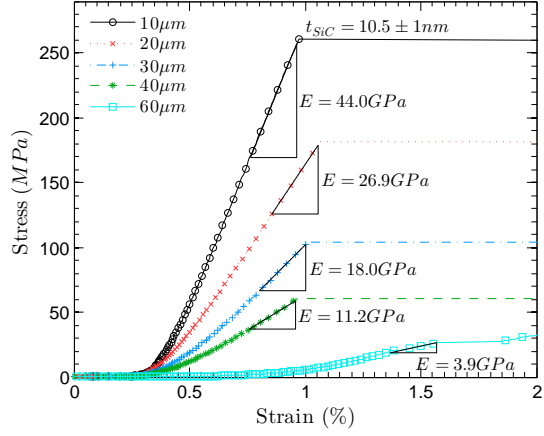


FIG. 5: Compressive failure of CNT pillars coated with 21.4 *nm* a-SiC.

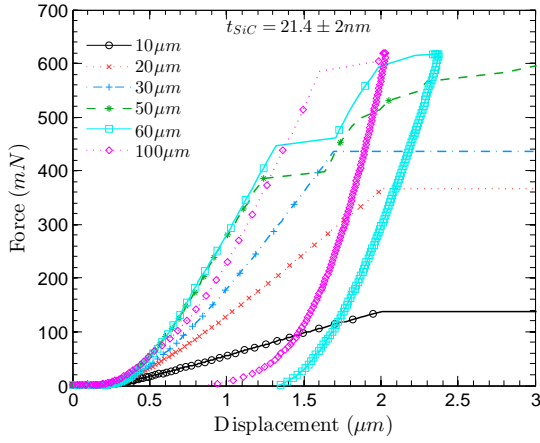
208 deduced from roughly 99% to 79% (Supplementary A3) and the bending stiffness of the highly
 209 flexible CNTs inside the pillar is increased. Moreover, the contribution from normal forces or
 210 stiffness originating from CNT fiber extension and compression becomes more significant as
 211 coating thickness increases. The coating interlocks and constrains the interwoven CNTs at
 212 their junctions. With a thicker coating, a larger distance between the CNTs can be bridged,
 213 subsequently bonding more CNTs together and reducing the porosity. As a consequence,
 214 the mechanical response of coated CNT arrays changes from foam-like, towards bamboo-like



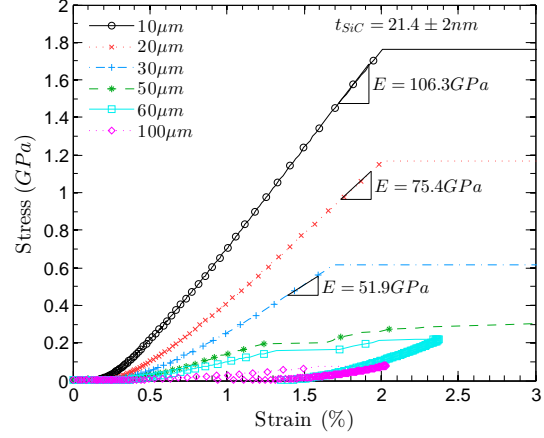
(a) 10.5 nm thick a-SiC coating.



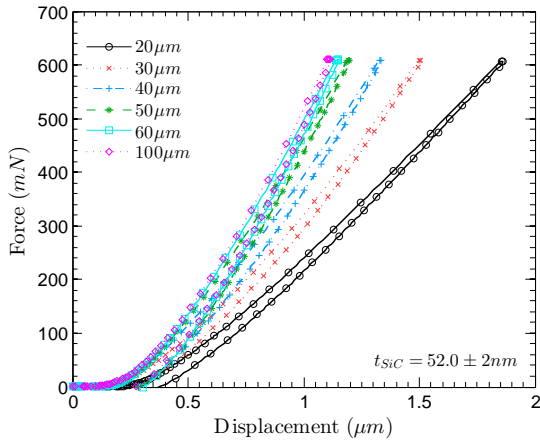
(b) 10.5 nm thick a-SiC coating.



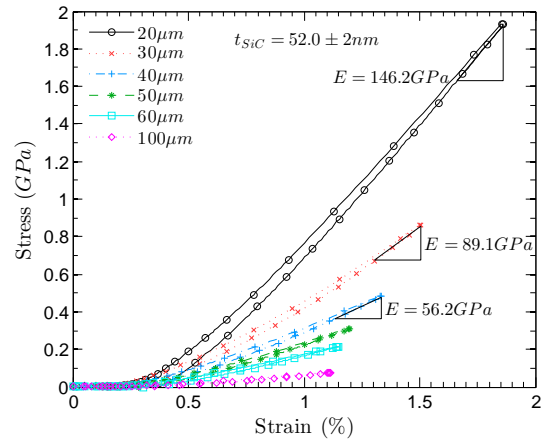
(c) 21.4 nm thick a-SiC coating.



(d) 21.4 nm thick a-SiC coating.



(e) 52.0 nm thick a-SiC coating.



(f) 52.0 nm thick a-SiC coating.

FIG. 6: Mechanical response of CNT pillars with a 10.5 nm, 21.4 nm and a 52.0 nm thick a-SiC coating. (a,c,e) The measured load versus displacement and (b,d,f) the engineering stress versus strain response.

215 and finally brittle-ceramic-like as coating thickness increases. A coating thickness gradient
 216 will cause the effective mechanical material properties of the pillar to strongly increase in
 217 radial direction from the centre. Thus, explaining the diameter dependency of the mate-
 218 rial properties of the coated pillars and drawing additional similarities with other types of
 219 orthotropic materials such as wood or bamboo.

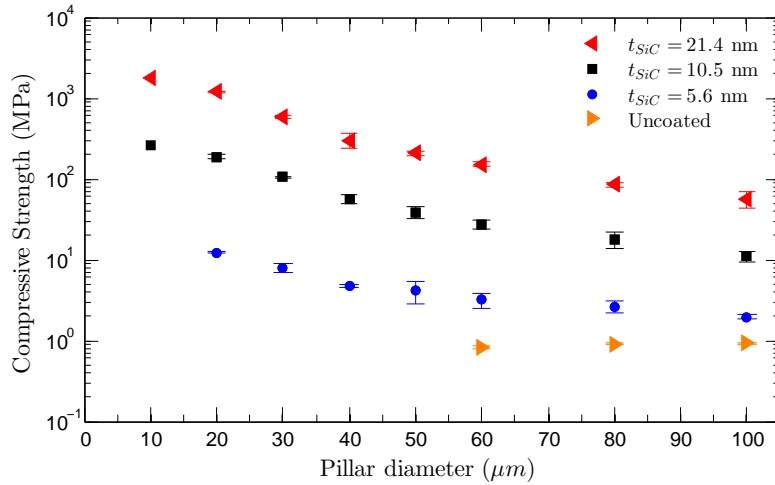


FIG. 7: Compressive failure stress of coated and uncoated pillars.

220 C. Young’s modulus

221 The effects of thin conformal a-SiC coatings on E the Young’s modulus of CNT pillars
 222 are measured using the continues stiffness measurement (CSM) mode of the nanoindenter
 223 (Supplementary Fig. A5). The uncoated samples and those with a thin a-SiC coating of
 224 5.6 nm have all collapsed before a plateau region was reached (Fig. S7a and Fig. S7b).
 225 The effective Young’s modulus of coated pillars increases drastically with increasing coating
 226 thickness. We find that the Young’s modulus increases with compression depth and plateau
 227 regions are observed for samples with 10.5 and 21.4 nm thick a-SiC coatings. The measured
 228 moduli in Fig. S7 are in excellent agreement with the moduli extracted from the slope of
 229 the stress-strain curves before failure occurs, see Fig. 6b and Fig. 6d, respectively. Another
 230 observation shows that E increases for coated pillars of smaller diameter, following the
 231 same trend as the compressive strength Fig. 7. A gradient in the coating thickness as
 232 a function of the surface penetration depth can be a possible explanation for the observed

233 pillar diameter dependency of the compressive strength and Young’s modulus measurements,
234 Supplementary [A 2](#) gives a more in depth analysis.

235 **III. CONCLUSIONS**

236 Carbon nanotube pillars were grown and their mechanical response was modified from
237 foam like towards brittle ceramic behavior, using a straightforward process of depositing
238 nanoscale conformal coatings of amorphous silicon carbide (a-SiC) by low pressure chemical
239 vapor deposition. The failure mode of coated pillars was characterized using nanoindentation
240 with a flat cylindrical punch. The dominant failure mode changed from localized periodic
241 buckling towards bamboo-like failure and finally towards brittle ceramic failure as coating
242 thickness increased. Vertical cracks at the exterior of the pillar were induced when the
243 circumferential stress exceeded the composite strength during compression. We conclude
244 that conformal coatings reduce the porosity of the array and increase the stiffness of the
245 highly flexible CNTs. Furthermore, the connections between neighboring tubes inside the
246 CNT array are increased and changed from weak van der Waals interaction for the uncoated
247 arrays, towards a bonded a-SiC connection.

248 As a result, a tremendous increase of 3 orders of magnitude for the Young’s modulus
249 and compressive strength of pillars with a 21.4 nm thick deposition of a-SiC was achieved.
250 The Young’s moduli increased from 200 MPa for uncoated pillars at 1 μm compression depth
251 towards a high value of about 125 GPa for a 10 μm diameter pillar with a thin conformal
252 coating of 21.4 nm a-SiC. Furthermore, the compressive strength of uncoated pillars increased
253 from values below 1 MPa towards a maximum of 1.8 GPa. We therefore propose that the
254 fast growing, conformal coated, CNT arrays can be useful as a strong structural material
255 for creating robust high aspect ratio 3D-micro architectures.

256 **IV. EXPERIMENTAL SECTION**

257 *CNT Growth:* The first step in the synthesis of different aspect-ratio CNT pillars consists
258 of growing a 170 nm thick thermal silicon oxide layer on a silicon wafer substrate to prevent
259 diffusion of the metal catalyst into the substrate. Next, a 15 nm thin layer of alumina (Al_2O_3)
260 is sputtered on the substrate to increase the CNT nucleation density from the catalyst

261 particles [50]. For the lift-off process we spin coat and pattern, using optical lithography,
262 a film of 1.5 μm thick negative photo-resist (AZ Nlof2000). Then a 2 nm thin layer of iron
263 (Fe) catalyst is deposited on the Al_2O_3 film by electron beam evaporation. The catalyst is
264 patterned by a lift-off process using a NMP ($\text{C}_5\text{H}_9\text{NO}$) solvent at 70 $^\circ\text{C}$ for dissolving the
265 resist. Next, (100 ± 2) μm tall vertically aligned multi-wall CNTs are grown in 5 minutes
266 by low pressure chemical vapour deposition (LPCVD) in a commercial deposition system
267 (Black Magic Pro, Aixtron). The CNTs are grown at a temperature of 600 $^\circ\text{C}$ using a gas
268 flow mixture of 700 sccm hydrogen over 50 sccm acetylene ($\text{H}_2/\text{C}_2\text{H}_2$) at 80 mbar.

269 *Conformal Coating:* The a-SiC films are deposited inside a Tempress hot-wall LPCVD
270 furnace using dichlorosilane (SiH_2Cl_2) and acetylene (C_2H_2) as gas precursor diluted at 5%
271 in hydrogen (H_2). The deposition temperature and pressure are set to 760 $^\circ\text{C}$ and 1 mbar,
272 respectively. The gas flow rates are 65 sccm SiH_2Cl_2 over 435 sccm C_2H_2 in 5% H_2 . A
273 detailed description of different SiC deposition process recipes and their characterization is
274 described in previous work [38].

275 *Mechanical Characterization:* The mechanical response of CNT pillars is characterized
276 using nanoindentation with an Agilent MTS Nanoindenter XP G200. Uniaxial compression
277 of the CNT pillars was achieved by using a 150 μm diameter custom made flat-punch diamond
278 indenter tip. For each test we detect the surface on a neighbouring pillar to avoid affecting
279 the pillar on which measurements are performed. Force, displacement and stiffness data were
280 acquired using the continuous stiffness measurement (CSM) technique. The CSM settings
281 used are: 2 nm amplitude, 45 Hz frequency, sensitive 100 N m^{-1} surface detection and a strain
282 rate of 0.01 s^{-1} .

283 SUPPORTING INFORMATION

284 Supporting Information is available from the Wiley Online Library or from the author.

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288 the Charged Particle Optics group for the Verios 460 extreme-high-resolution (XHR) SEM

289 support.

290 **Appendix A: Supporting Information**

291 **1. CNT sample preparation**

292 The synthesis of different aspect-ratio CNT pillars is illustrated in Fig. S1a. The first step
293 consists of growing a 170 nm thick thermal silicon oxide layer on a silicon wafer substrate
294 to prevent diffusion of the metal catalyst into the substrate. Next, a 15 nm thin layer
295 of alumina (Al_2O_3) is sputtered on the substrate to increase the CNT nucleation density
296 from the catalyst particles [50]. Then a 2 nm thin layer of iron (Fe) catalyst is deposited
297 on the Al_2O_3 film by electron beam evaporation. The catalyst is patterned using optical
298 lithography and a lift-off process Fig. S1b. For the lift-off process we spin coat a film of
299 1.5 μm thick negative photo-resist (AZ Nlof2000) and use a NMP ($\text{C}_5\text{H}_9\text{NO}$) solvent at 70 °C
300 for dissolving the resist during the lift-off. Next, (100 ± 2) μm tall vertically aligned multi-
301 wall CNTs are grown in 5 minutes by low pressure chemical vapour deposition (LPCVD)
302 in a commercial deposition system (Black Magic Pro, Aixtron) (Fig. S1c). The CNTs are
303 grown at a temperature of 600 °C using a gas flow mixture of 700 sccm hydrogen over 50
304 sccm acetylene ($\text{H}_2/\text{C}_2\text{H}_2$) at 80 mbar.

305 **2. CNT coating procedure**

306 The CNT arrays are conformally coated with a-SiC to promote the interlocking of indi-
307 vidual CNTs at junctions, see Fig. S1d. Low pressure chemical vapour deposition (LPCVD)
308 allows for controlled deposition of very thin and conformal layers. The deposition param-
309 eters; temperature and ratio of precursor flows, were tuned in order to obtain amorphous
310 layers of silicon carbide (a-SiC). The slow rate of deposition of a-SiC improves the infiltration
311 of the precursor gases inside the porous CNT array. Poly-SiC layers have a higher deposition
312 rate and they tend to close the CNT array on the outer surface before complete infiltration
313 occurs. Hence, a-SiC deposition results in a more conformal layer deposited on the CNTs.

314 The a-SiC films are deposited inside a Tempress hot-wall LPCVD furnace using dichlorosi-
315 lane (SiH_2Cl_2) and acetylene (C_2H_2) as gas precursor diluted at 5% in hydrogen (H_2). The
316 deposition temperature and pressure are set to 760 °C and 1 mbar, respectively. The gas flow

317 rates are 65 sccm SiH_2Cl_2 over 435 sccm C_2H_2 in 5% H_2 . A detailed description of different
 318 SiC deposition process recipes and their characterization is described in previous work [38].

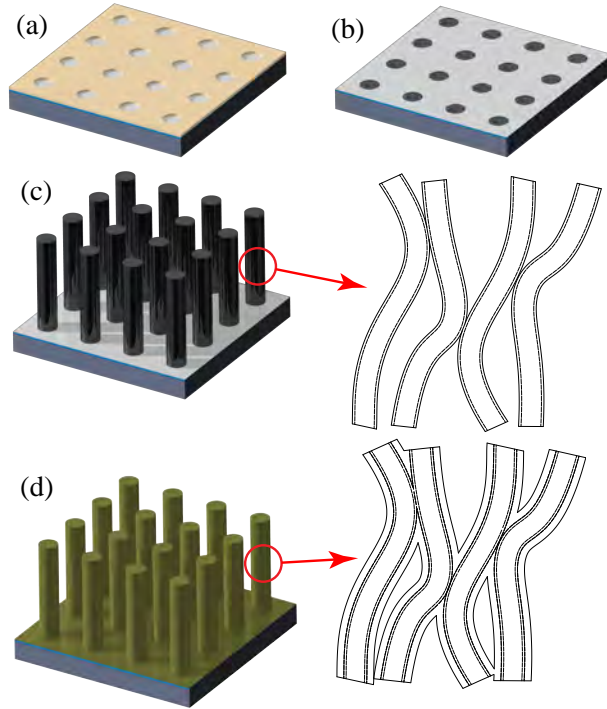


FIG. S1: Schematic illustration of the fabrication procedure. (a) Si substrate with thermal SiO_2 , sputtered Al_2O_3 and patterned photo-resist. (b) E-beam evaporation of Fe and lift-off procedure. (c) CNT growth and microstructure illustration. (d) Conformal amorphous-silicon carbide coating and the modified array microstructure.

319 The a-SiC layer thickness is controlled by careful timing of the deposition process. Bare
 320 silicon test wafers are added to the processing batch as reference. The layers are measured
 321 by variable angle spectroscopic ellipsometry using a Woollam M-2000UI[®] ellipsometer. The
 322 spectra are obtained at 7 different angles between 45° and 75° , in the spectral range of
 323 245 nm and 1690 nm. The reference measurement on bare Si wafers is used as an estimation
 324 of the deposited a-SiC thickness on the CNTs. The deposition times that correspond with
 325 a film thickness of 5.6 nm, 10.5 nm, 21.4 nm and 52.0 nm is respectively 18 min, 28 min,
 326 50 min and 120 min, see Fig. S2. From the linear fit we estimate a deposition rate of about
 327 5 \AA min^{-1} . Furthermore, we have confirmed t_{inc} , an incubation time of about 7 min before
 328 the films starts growing. It should be noted that the incubation time and therefore the final
 329 thickness of a-SiC on CNTs might be different than a-SiC on bare silicon test wafers due to

330 the difference in substrate material. In addition, the porous CNT pillars have a large surface
 331 area to volume ratio. The gas precursors in LPCVD react with the surface they come into
 332 contact with. Therefore, the concentration of precursor reactants inside the CNT array can
 333 reduce when the gas infiltrates the CNT pillar further. Consequently, this might lead to a
 334 reduction of the deposition rate of a-SiC inside the bundle. As a result, pillars with larger
 335 diameters can have a thinner layer of a-SiC deposited on the inside of the pillar than on the
 336 outside.

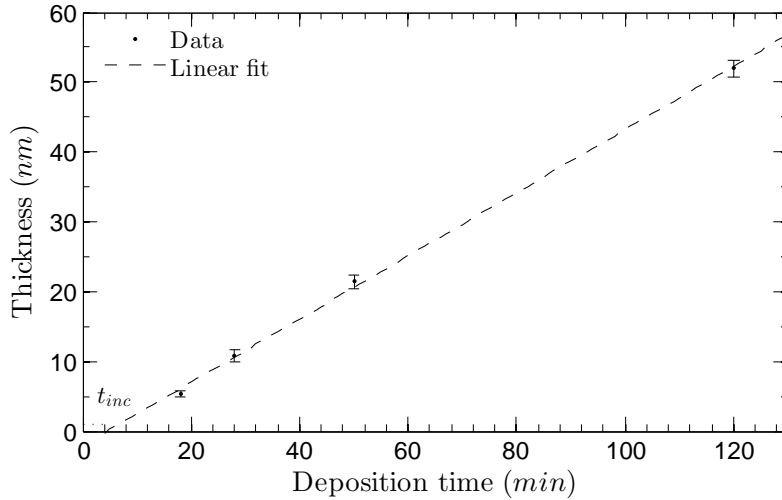


FIG. S2: Ellipsometer measurements of the LPCVD a-SiC film thickness on bare silicon test wafers versus deposition time. The dots are the measured data the broken line represent the expected values generated from a linear fit. The data suggests the presence of an incubation time t_{inc} before the films starts growing in thickness.

337 The coating penetration depth and thickness is investigated by splitting the 10.5 nm
 338 a-SiC coated micropillars with a Berkovich tip, see Fig. S3a-b. A Verios 460 extreme-high-
 339 resolution (XHR) SEM is used to perform an investigation on the coating inside the pillar.
 340 The first observation is that the coating appears to penetrate the bundle fully, however the
 341 coating thickness decreases for increased penetration depth. The coated CNT bundles near
 342 the outer surface of the pillar have an average diameter of about 30 nm (Fig. S3d), the
 343 uncoated CNTs have an average diameter of about 9 nm (Fig. S4). Therefore the coating
 344 thickness t_{SiC} on the CNTs is about 10.5 nm which is in excellent agreement with the film
 345 thickness measured by ellipsometry on bare Si test wafers. Moving 20 μm deeper inside the
 346 pillar, we notice that the average coating thickness is reduced to about 6.5 nm (Fig. S3e).

347 At 40 μm penetration depth, the coating thickness is reduced to about 5 nm (Fig. S3f).

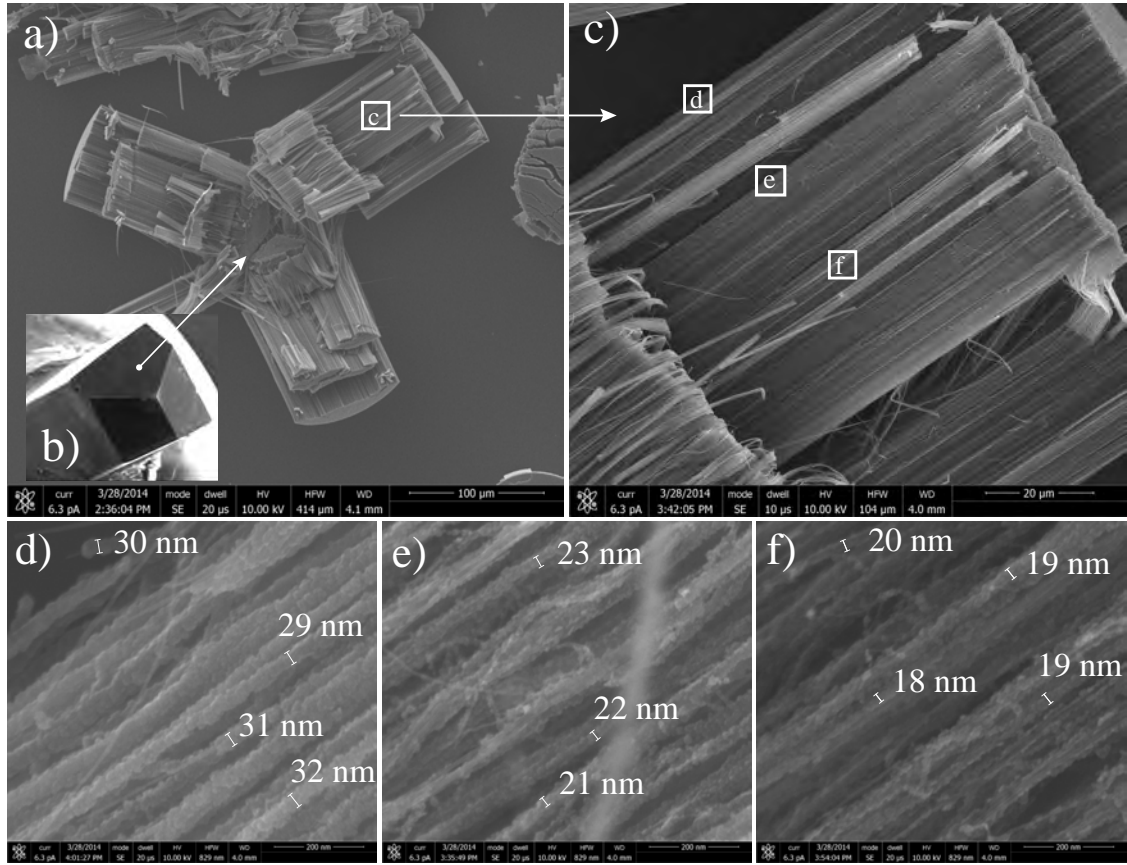


FIG. S3: (a) CNT pillar (100 μm diameter) with 10.5 nm a-SiC coating, cleaved with (b) a Berkovich nanoindentation tip. (c) Location used for investigation of the coating penetration depth. (d) Coating thickness of CNTs near the outer surface of the pillar. (e) Coating thickness at 20 μm distance from the surface. (f) Coating thickness at 40 μm distance from the surface.

348 3. Correlation between coating thickness and porosity

349 The density of the uncoated CNT array is about $n = 10^{10} \text{ tubes}/\text{cm}^2$. Other researchers
 350 have reported similar densities in the order of 10^{10} to $10^{11} \text{ tubes}/\text{cm}^2$ [4, 9, 51]. It should
 351 be noted that the density is very difficult to determine accurately and it is a very rough
 352 estimation. Fig. S4 shows that the average CNT diameter D_{cnt} is about 9 nm. Calculating
 353 the cross-sectional area of a single CNT using,

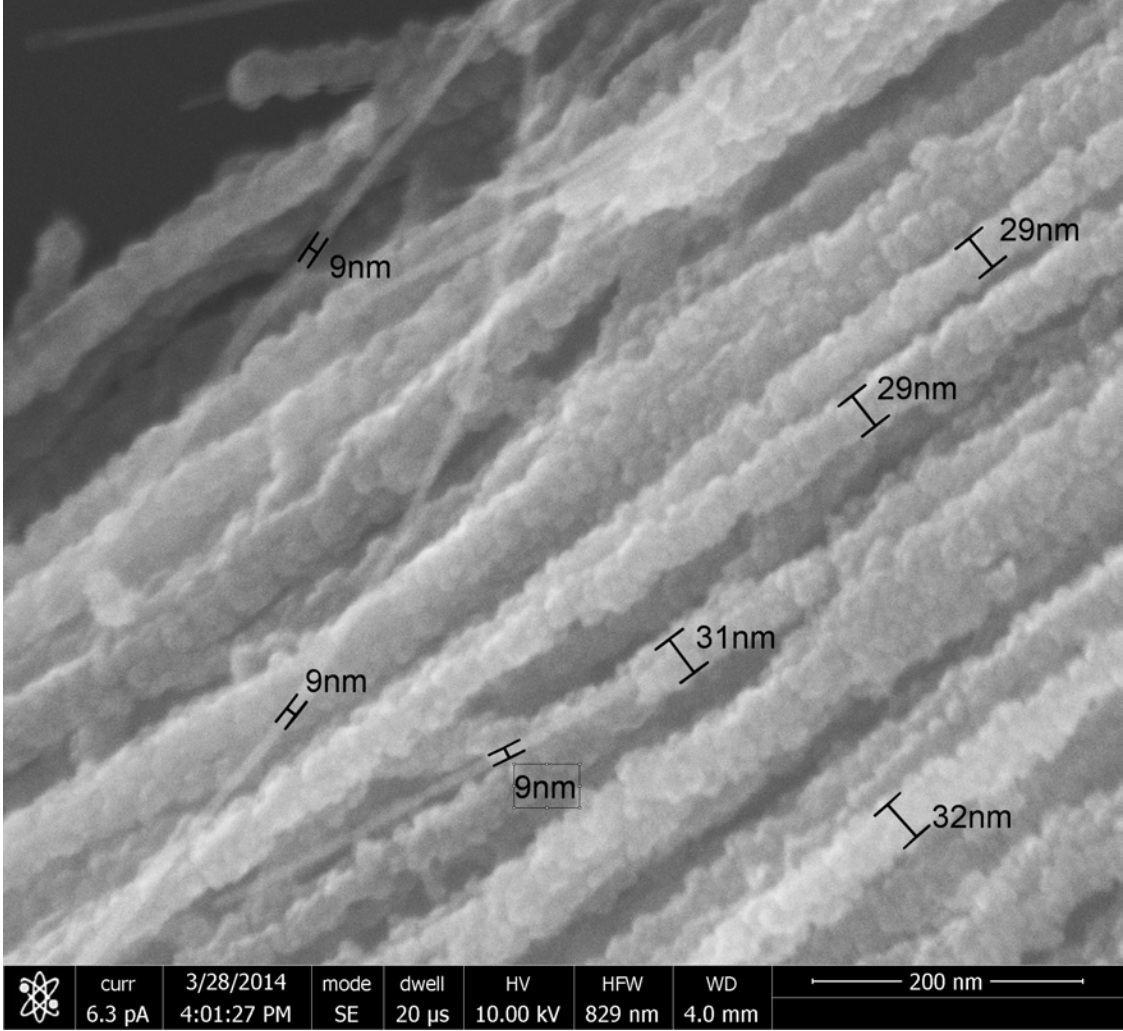


FIG. S4: Surface of a broken CNT pillar with a 10.5 nm thick conformal a-SiC coating, showing CNTs sticking out of the broken matrix.

$$A = \frac{\pi}{4}(D_{cnt} + 2t_{SiC})^2, \quad (\text{A1})$$

we can determine the porosity as a function of the coating thickness, see Tab. S1. The measured properties of the a-SiC coated CNT pillars is just a fraction of the intrinsic properties of SiC due to the high porosity. The intrinsic SiC Youngs modulus ranges from 200 to 544 GPa, while the hardness ranges from 20 to 50 GPa [37, 39, 52–54]. Since the corrected material properties are strongly dependent on the porosity, and since the porosity is difficult to determine accurately, we think that the corrected bulk modulus can be inaccurate. A more useful property for engineering purposes, may be the measured effective Young’s

TABLE S1: Pillar surface porosity and properties as function of the coating thickness.

Coating thickness $t_{SiC}(nm)$:	0	5.6	10.5	21.4
Porosity $p(\%)$:	99.4	96.8	92.9	78.9

361 modulus of the coated CNT arrays which we reported in the article in Fig. S7.

362 4. Raman spectroscopy

363 To determine the quality of the CNTs and the effects of a-SiC deposition we perform a
 364 Raman characterization using a Renishaw inVia system with a 514 nm wavelength Ar+ laser.
 365 Fig. S5 shows the Raman spectrum of the CNT arrays before and after a-SiC deposition.
 366 All curves are normalized towards the (G) peak amplitude and vertically offset.

367 Deposition of a-SiC directly on an oxidized Si substrate in curve (a) in Fig. S5, shows a
 368 sharp feature at 520 cm^{-1} and a smaller feature around 970 cm^{-1} which originate from the
 369 crystalline Si substrate. The weak bump near 1475 cm^{-1} can be connected to the presence of
 370 unprocessed acetylene used in the a-SiC deposition [55]. Fig. S5 curve (b) shows the Raman
 371 spectrum intensity of the as-grown CNT array, the peaks near 1580 cm^{-1} and 1350 cm^{-1} in
 372 the first order region correspond with the graphite (G) and disordered graphite (D) modes
 373 of the CNTs [51, 56–58]. The (G) peak has convolved with a shoulder peak at 1620 cm^{-1} ,
 374 which is known as the (D') peak and is associated with graphite crystals and graphene edges
 375 which was fitted to a Gaussian curve. The intensity of the disordered graphite peak refers
 376 to the amount of micro crystalline graphite present inside the tube. The ratio I_G/I_D of the
 377 intensity peaks can be used to evaluate the quality of the CNTs, a higher ratio indicates
 378 a better quality. Curves (c), (d) and (e) are CNTs coated with a-SiC with an increasing
 379 film thickness. The location and amplitude of the deconvolved peaks were determined from
 380 fitted Lorentzian curves at 1350 and 1580 cm^{-1} and Gaussian curves at 1475 and 1620 cm^{-1} .

381 5. Nanoindentation measurements

382 The effects of a-SiC coatings on the mechanical response of CNT pillars is characterized
 383 using nanoindentation with an Agilent MTS Nanoindenter XP G200. Uniaxial compression
 384 of the CNT pillars was achieved by using a $150\text{ }\mu\text{m}$ diameter custom made flat-punch diamond

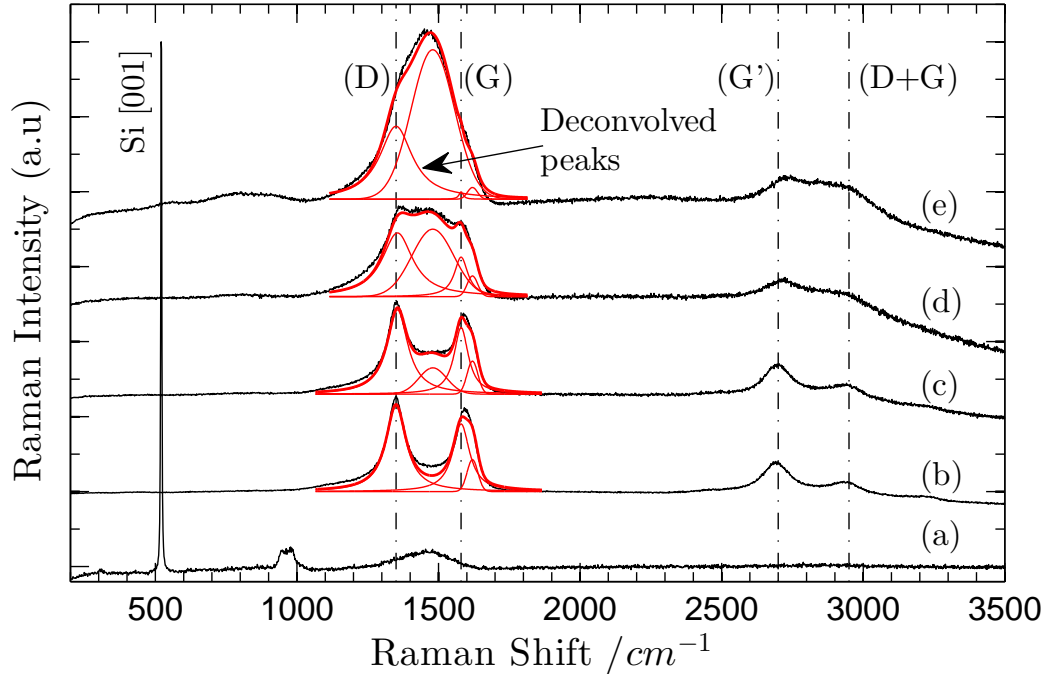


FIG. S5: Raman spectra intensity measurement with a 514 nm wavelength Ar+ laser normalized with respect to the graphite (G) mode. (a) Silicon substrate with 21.4 nm a-SiC. (b) As-grown CNT array. (c,d,e) CNT arrays with 5.6 nm, 10.5 nm, 21.4 nm and 52.0 nm a-SiC coating respectively.

385 indenter tip. A schematic illustration is shown in Fig. S6a. The pillars were compressed until
 386 failure occurs in the form of buckling or fracture, then unloading is initiated. The tested
 387 pillars have an average height of about $(100 \pm 2) \mu\text{m}$ and diameters ranging from $(10 \pm 1) \mu\text{m}$
 388 to $(150 \pm 1) \mu\text{m}$, see Fig. 1a. The coated samples were prepared with respectively, 5.6 nm,
 389 10.5 nm, 21.4 nm and 52.0 nm thin, conformal coatings of a-SiC using LPCVD.

390 The flat surface of the tip allows for accurate detection of the CNT pillar surface and keeps
 391 a uniform contact area during compression [48]. For each test we detect the surface on a
 392 neighbouring pillar to avoid affecting the pillar on which measurements are performed. Force,
 393 displacement and stiffness data were acquired using the continuous stiffness measurement
 394 (CSM) technique. The main advantages of this technique are the continuous measurement
 395 of contact stiffness S_m as a function of depth δ , this eliminates the need for unloading cycles.
 396 The method relies on applying a small harmonic load with frequency ω on the nominal load.
 397 The CSM settings used are: 2 nm amplitude, 45 Hz frequency, sensitive 100 N m^{-1} surface
 398 detection and a strain rate of 0.01 s^{-1} . The measured contact stiffness S_m has been corrected

399 for S_f the indenter frame stiffness, S_t the diamond tip stiffness and S_s the substrate stiffness
 400 by modelling the entire system as springs in series, see Fig. S6b, and applying Eq. (A2)
 401 which gives S_p the pillar stiffness,

$$S_p = \frac{1}{1/S_m - 1/S_f - 1/S_t - 1/S_s}. \quad (\text{A2})$$

402 The relationship between E the Young's modulus and S the contact stiffness is often
 403 given by *Sneddon's* relationship [59], see Eq. (A3) in this paper. However, this equation is
 404 more accurate when an elastic half space is compressed with a rigid flat-cylindrical punch.
 405 In this case the stresses are not uniform. In our case where relatively compliant pillars
 406 are compressed, the assumption of uniaxial compression and uniform stress becomes more
 407 accurate for the pillar, while *Sneddon's* relationship is more suitable for the substrate and
 408 tip. The stiffness of the silicon substrate and the diamond tip are therefore modelled as
 409 an elastic half-space which is being compressed with a flat spherical cylinder see Fig. S6b.
 410 The substrate and tip stiffnesses are directly proportional to pillar diameter and Young's
 411 modulus, see Eq. (A3). In the computation of S_s and S_t (Eq. (A3a) and Eq. (A3b)), we
 412 use $E_s = 130$ GPa and $\nu_s = 0.28$ for the Young's modulus and Poisson's ratio of the silicon
 413 substrate and $E_t = 1.2$ TPa and $\nu_t = 0.2$ for the diamond tip. The frame stiffness S_f , is
 414 a calibrated property and remains constant regardless of pillar diameter. The contact area
 415 $A = \pi D^2/4$, between the tip and the pillar is in our case defined by D the pillar diameter.
 416 The real surface contact area is lower and defined by the occupation fraction of the CNTs
 417 inside the array as well as the roughness of the pillar surface [9]. To simplify the computation
 418 of the material properties we assume constant contact area during compression and calculate
 419 the effective properties from the measured data.

$$S_s = \frac{2E_s}{1 - \nu_s^2} \sqrt{\frac{A}{\pi}} = \frac{E_s D}{1 - \nu_s^2} \quad (\text{A3a})$$

$$S_t = \frac{2E_t}{1 - \nu_t^2} \sqrt{\frac{A}{\pi}} = \frac{E_t D}{1 - \nu_t^2} \quad (\text{A3b})$$

420 After substitution of Eq. (A3a) and Eq. (A3b) for S_s and S_t into Eq. (A2) and solving for
 421 S_p the stiffness of the CNT pillars, we can compute the Young's modulus of the pillar using
 422 Eq. (A4). When S_p the sample stiffness approaches the stiffness of the measurement setup
 423 the corrections to S_m the measured stiffness become more significant, this occurs for large

424 diameter pillars with thick coatings. Henceforth we have taken the maximum measured
 425 pillar stiffness to perform a sensitivity analysis. The maximum corrections are 1%, 4%, 15%
 426 and 30% for uncoated and coated 100 μm diameter pillars with film thickness of 5.6 nm,
 427 10.5 nm, 21.4 nm and 52.0 nm , respectively.

$$E_p = \frac{4S_p L}{\pi D^2}. \quad (\text{A4})$$

428 Engineering stress σ and strain ϵ are computed from F the measured nanoindentation
 429 load, δ the tip displacement, L the undeformed pillar height and D the pillar diameter,

$$\sigma = \frac{F}{\pi D^2/4}, \quad \epsilon = \frac{\delta}{L} \quad (\text{A5})$$

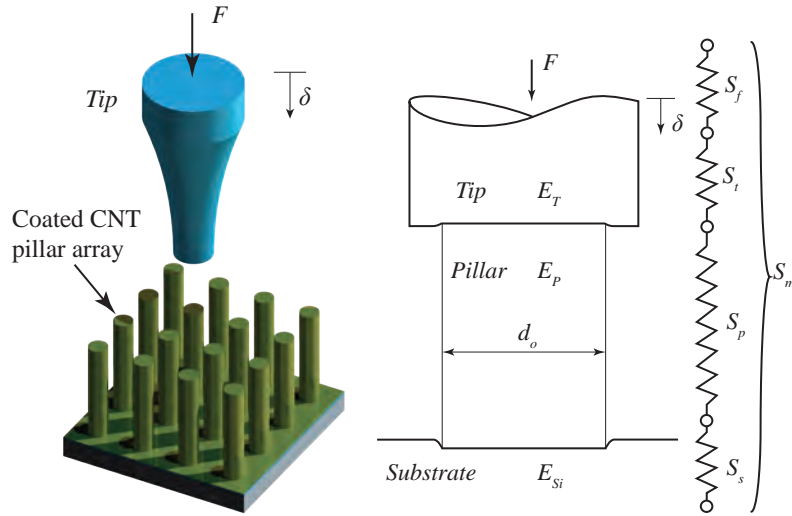
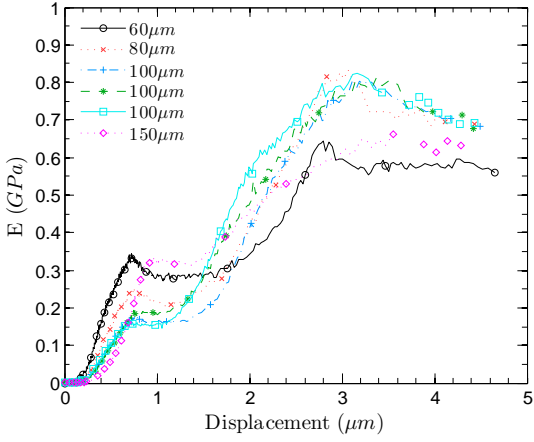
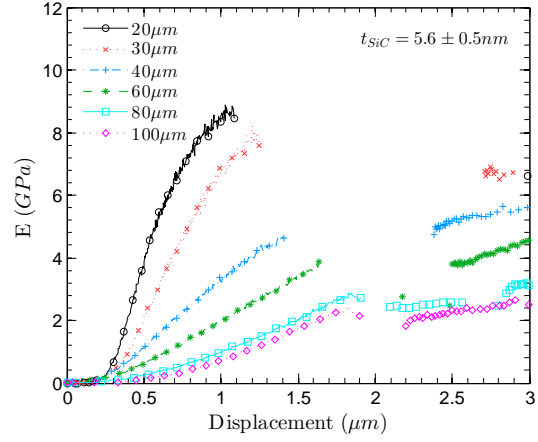


FIG. S6: Schematic illustration of (a) the flat-tip nanoindentation procedure, (b) the contact mechanics between indenter tip, pillar and substrate together with an equivalent spring model.

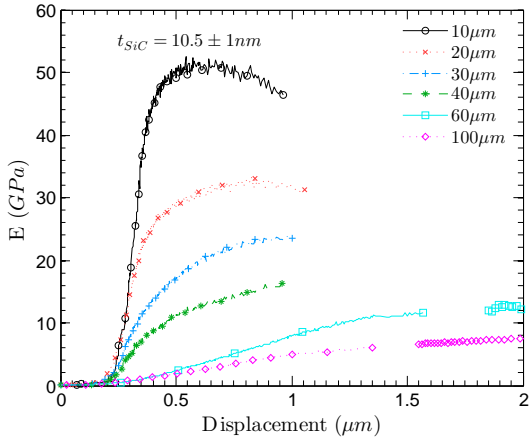
430 The effects of thin conformal a-SiC coatings on E the Young's modulus of CNT pillars are
 431 shown in Fig. S7. The results are discussed in IIC. The pillar stiffness was measured using
 432 the continues stiffness measurement (CSM) mode of the nanoindenter and the respective
 433 Young's moduli is calculated using Eq. (A4).



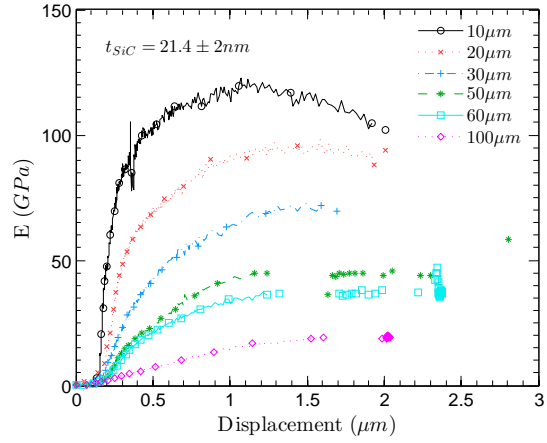
(a) As grown CNT pillars.



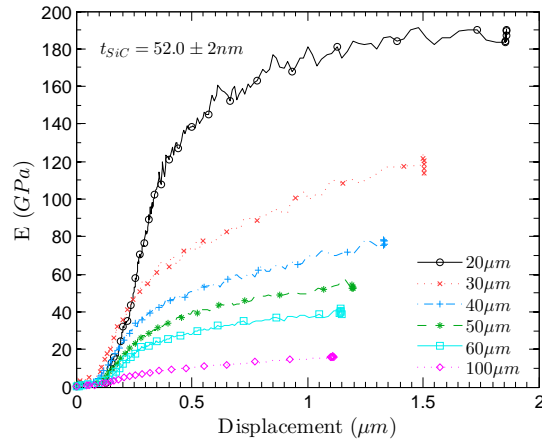
(b) with a 5.6 nm thick SiC coating.



(c) with a 10.5 nm thick SiC coating.



(d) with a 21.4 nm thick SiC coating.



(e) with a 52.0 nm thick SiC coating.

FIG. S7: Effective Young's modulus of coated and uncoated CNT pillars with diameters ranging from 10 to 150 μm as a function of displacement.

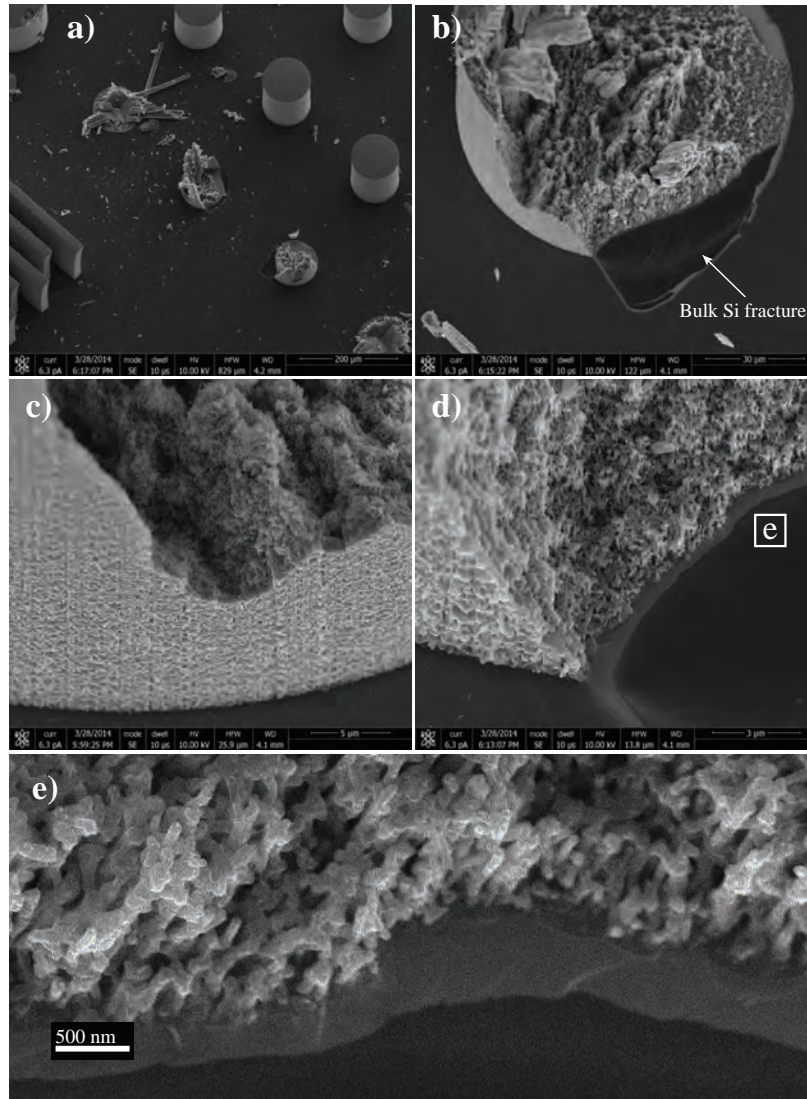


FIG. S8: Compressive failure of pillars coated with 52.0 nm a-SiC. The pillars could only be broken with a Berkovich nanoindentation tip.

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