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BRIEF TECHNICAL NOTE

Large-Displacement Indentation Testing of Vertically Aligned Carbon Nanotube Arrays

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Abstract Mechanical properties and deformation of the vertically aligned carbon nanotube arrays (VA-CNTs) has been examined with large-displacement indentation tests inside a scanning electronic microscope (SEM). The *in-situ* indentation allows for establishment of the load-depth responses and real-time observations of the deformation processes. Under a cylindrical, flat indenter, the VA-CNTs exhibit elastic deformation at small displacement and then plastic deformation at large displacement. The critical indentation pressure (P_m), a measure of collapsing stress of the CNT arrays, is obtained. The magnitude of P_m is approximately equal to the collapsing stress of the carbon nanotube arrays obtained under uniaxial compression.

Keywords Vertically aligned carbon nanotubes · Indentation · Large deformation

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Introduction

Vertically aligned carbon nanotube arrays (VA-CNTs) have received considerable attention lately due to their unique structures and potential applications. A thorough understanding of the mechanical behaviors of the VA-CNTs is important from the design point of view. The small strain, elastic responses of the CNTs have been studied, mostly through conventional, elastic nanoindentation tests [1–3]. The deformation behaviors of the VA-CNTs at large strain have been investigated recently through compressive testing [4–6]. Under compression, the CNT arrays behave as an open-cell foam-like material, folding themselves in wavelike pattern. The wavelike folding has been observed to always initiate at the bottom of the CNT arrays and then to propagate towards the top. The compressive deformation of the CNTs has been further analyzed through numerical simulations [7]. This paper reports the large-displacement deformation of the VA-CNT arrays by *in-situ*, deep indentation test, with the goals to characterize the plastic properties of the CNT arrays and relevant deformation mechanism.

The large-displacement indentation test has been a proved method for examining the plastic deformation of materials in small volumes [8–10]. Cylindrical, flat tip geometry is typically used for the indenter. Compared to indenters of parabolic and three-face pyramidal shapes, the contact area of a cylindrical flat indenter does not change with displacement, and the extent of the stress field scales with the diameter of the indenter [11]. The present experiments were conducted with an *in-situ* nanoindenter equipped inside the scanning electronic microscope chamber, which revealed both quantitative information (load–displacement) and phenomenological behaviors of the CNT arrays.

Large Displacement Indentation Experiments and Results

The VA-CNTs were synthesized by low pressure chemical vapor deposition (CVD) of acetylene on planar substrates (SiO_2/Si wafers). The catalyst coated substrates were inserted into the quartz tube furnace at 750°C in air for 10 min, followed by pumping the furnace chamber to a pressure less than 1.3 Pa. The growth of the CNT arrays was achieved by flowing a mixture gas of 48% Ar, 28% H_2 and 24% C_2H_2 for 10–20 min. The VA-CNTs were multiwalled (2–3 walls) carbon nanotubes and had a narrow uniform diameter distribution between 10 and 20 nm. The area density of the CNT arrays was estimated as: $\rho=10^{10}\sim10^{11}$ tubes/cm^2. Figure 1 shows the side views of a 215 μm tall CNT arrays.

The large-displacement indentation tests were conducted on as-grown VA-CNTs with a custom designed *in-situ* nanoindenter equipped inside the SEM (FEI Sirion). The sizes (heights) of the specimens were chosen carefully to avoid the influence of rigid substrates. The stress field beneath a cylindrical, flat indenter is typically confined within one indenter diameter. Given the size of current indenter (100 μm in diameter), the CNT specimens with heights bigger than 100 μm were used. When a cylindrical indenter of radius a is pressed onto a CNT arrays, the total load (L_{total}) acting on the indenter is the sum of the axial load acting on the indenter end face (L_a) and the frictional load acting on the indenter side wall (L_f). The mean indentation pressure acting on the indenter end is expressed as $P_m=L_a/\pi a^2$. The frictional load (L_f) on the indenter side wall is defined by $L_f=2\pi a d\tau$, where τ is the frictional shear stress and d the contact depth.

$$L_{total} = L_a + L_f \tag{1}$$

$$\frac{L_{total}}{\pi a^2} = P_m + \frac{2d}{a}\tau \tag{2}$$

The indentation stress- normalized displacement responses of two CNT arrays (215 μm and 1,100 μm in heights) are shown in Fig. 2. Two distinctive regimes can be observed in the indentation stress-displacement curves of the CNT arrays: a short elastic region and a plateau-like plastic region. The plateau region indicates the plastic collapses of carbon nanotubes beneath the indenter face. Such collapse allows the strain increase while the stress stays approximately constant. Since the force required for crushing additional nanotubes is relatively small (because its volume is a small fraction of the material under load), the measurement of the stress associated with the buckling movement are small. Therefore, the total stress at the large strain region has stayed relatively constant. Overall, the stress-displacement response of the CNT arrays is identical to that of an open-cell foam-like material [12, 13].

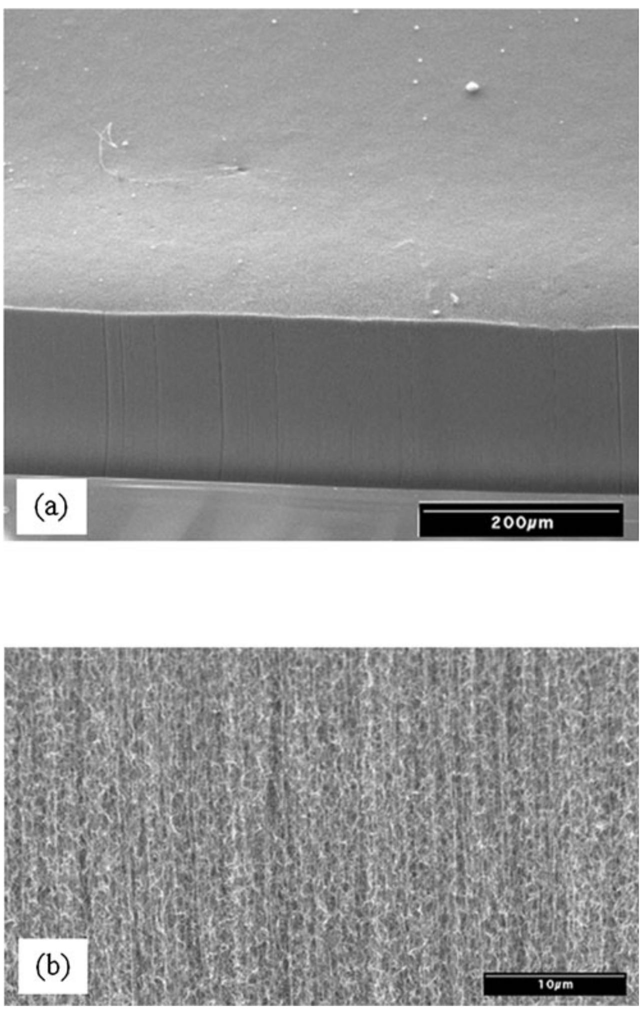

Fig. 1 SEM images showing the morphology of the side surafce of the vertically-aligned carbon nanotube arrays (t=215 μm)

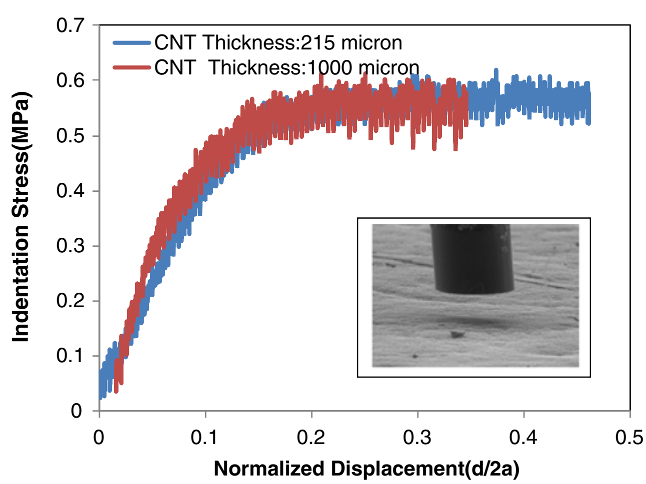

Fig. 2 Indentation stress-displacement curves of vertically aligned carbon nanotube arrays with cylindrical, flat-faced indenter

The normalized stress-displacement curve could then be used to estimate the critical indentation stress (P_m) and the frictional shear stress (τ). For the present CNT arrays, the slopes of stress-displacement at large displacements are almost zero (Fig. 2), indicating that the friction shear stress (τ) on the indenter wall due to the elastic compression from surrounding nanotubes is negligible. This is consistent with the finding reported by Tu et al. [14]. The critical indentation stress, P_m, is determined by extrapolating the large-strain indentation stress-displacement curve back to zero displacement (equation (2)). The magnitude of P_m so obtained for the present CNT arrays is approximately 0.56 MPa.

The same CNT arrays (t=215 μm) have been tested under uniaxial compression using the same *in-situ* testing apparatus (Fig. 3). The modulus is calculated from the initial portion of the stress–strain curve, E=6.8 MPa, consistent with the reported values for typical nanotue arrays [4]. The yield strength is taken as the maximum stress at the peak: σ_y=0.48 MPa. The critical indentation stress (P_m) is proportional to the uniaxial yield stress (σ_y) for a material through a constraint factor: $P_m = C \cdot \sigma_y$ [15]. The constraint effect is due to the confining pressure generated by the surrounding elastically strained material in the indentation stress field. Current results indicate that the critical value of the indentation stress, P_m, is very close to the uniaxial yield stress (σ_y) for the CNT arrays: $P_m/\sigma_y \approx 1.15$. For the foam-like CNT arrays with a plastic Poisson's ratio near zero, the large indentation has resulted in very little lateral spreading of the CNT fibers under the indenter. Thus, the constraint factor becomes unity.

The present *in-situ* nanodenter is equipped inside a SEM chamber, which allows for real-time observation and video recording of the deformation process while the CNT arrays are compressed (Fig. 4). The early stage of penetration is dominated by the elastic deformation. Further penetration of the indenter results in the plastic collapse of the carbon nanotubes immediately beneath the indenter head. Assuming that the CNT arrays are open-cell foam-like materials, the stress and strain fields under a flat indenter have been computed through finite element simulation. Figure 5 shows the resultant equivalent plastic strain (ε^{eq}) in the CNT arrays. ε^{eq} is defined by $\varepsilon^{eq} = \sqrt{\frac{2}{3}(\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_3^2)}$ and ε_1, ε_2, ε_3, are the principal strains. For ε^{eq}>0, the material has yielded. For CNT arrays or foam-like materials, the

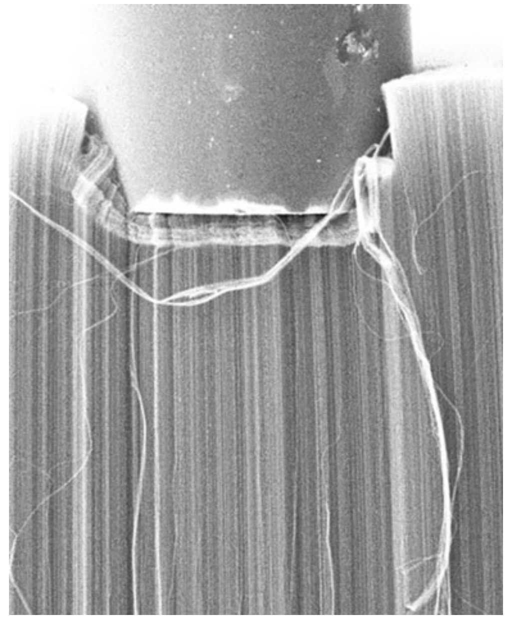

Fig. 4 SEM image showing the development of plastic collapsing of the vertically aligned carbon nanotube arrays under a flat cylindrical indenter (t=1,100 μm)

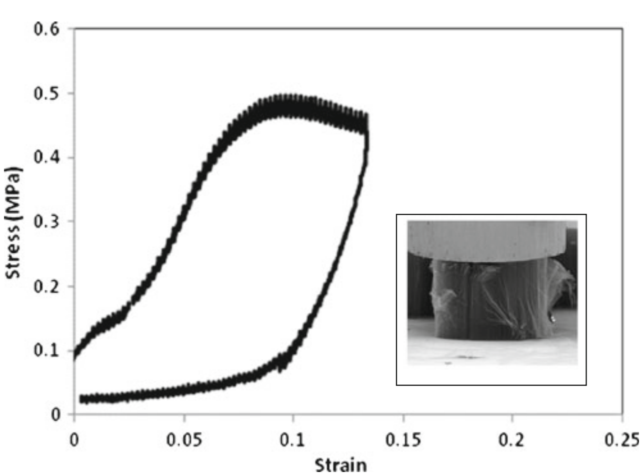

Fig. 3 Compressive stress–strain curve of the vertically aligned carbon nanotube arrays (t=215 μm)

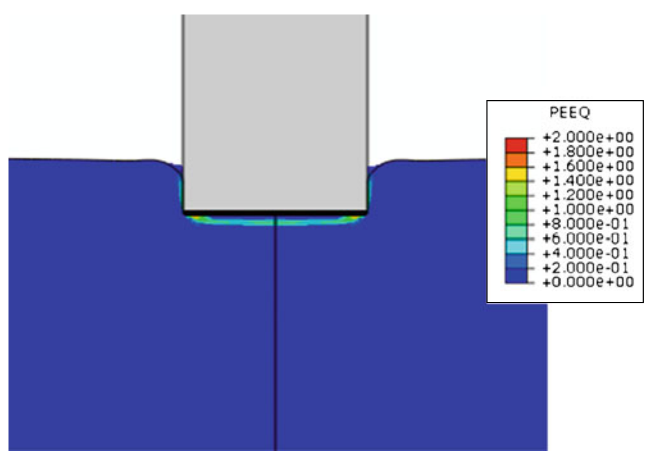

Fig. 5 Finite element calculation of equivalent plastic strain (ε^{eq}) in vertically aligned carbon nanotube array material. The material is treated as an open-cell foam-like material

highest strain is seen to occur right beneath the indenter face. The shape of this strain concentration zone is much narrower, as opposed to a larger, hemispherical zone observed in typical dense materials [8–10]. All these suggest that the CNT material would buckle/fold right before the indenter face and then propagates towards to the bottom, which is in contrast with the "bottom-to-top" deformation process occurred under axial compression [4, 5].

Conclusion

Mechanical properties and deformation of the vertically aligned carbon nanotube arrays have been studied through large-displacement indentation tests. Low speed, large-displacement indentation tests were first performed with *in-situ* indentation inside a SEM. The vertically aligned carbon nanotube arrays exhibit a transient elastic deformation at small displacement and then plastic deformation at large displacement. The critical indentation pressure (P_m) can be extrapolated from the indentation stress-displacement curve, which is a measure of the collapsing stress of CNT arrays. The magnitude of P_m at the end of the indenter is approximately equal to the collapsing stress of the same carbon nanotube array under uniaxial compression, indicating that there is negligible interfacial friction between the nanotubes and the indenter sidewall. Under the cylindrical, flat-ended punch, the nanotube cells collapsed plastically immediately beneath the indenter, a region of the highest stress/strain. The plastic deformation remained relatively unchanged in size at large displacement, corresponding to the plateau region on the load-depth curve.

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