Insights into Energy Absorption Mechanisms in Hierarchical Carbon Nanotube Forests

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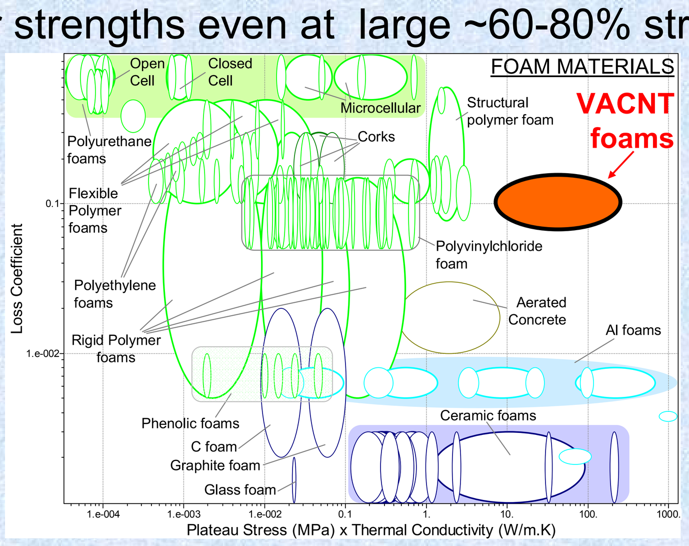
Introduction

VACNTs (vertically aligned carbon nanotubes) –

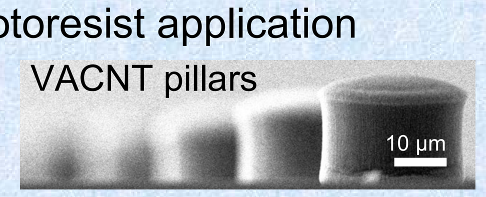
- unique hierarchical structure resulting in
- mechanical properties that combine the best of polymeric (high recoverability) and metallic foams (higher strengths even at large ~60-80% strains).



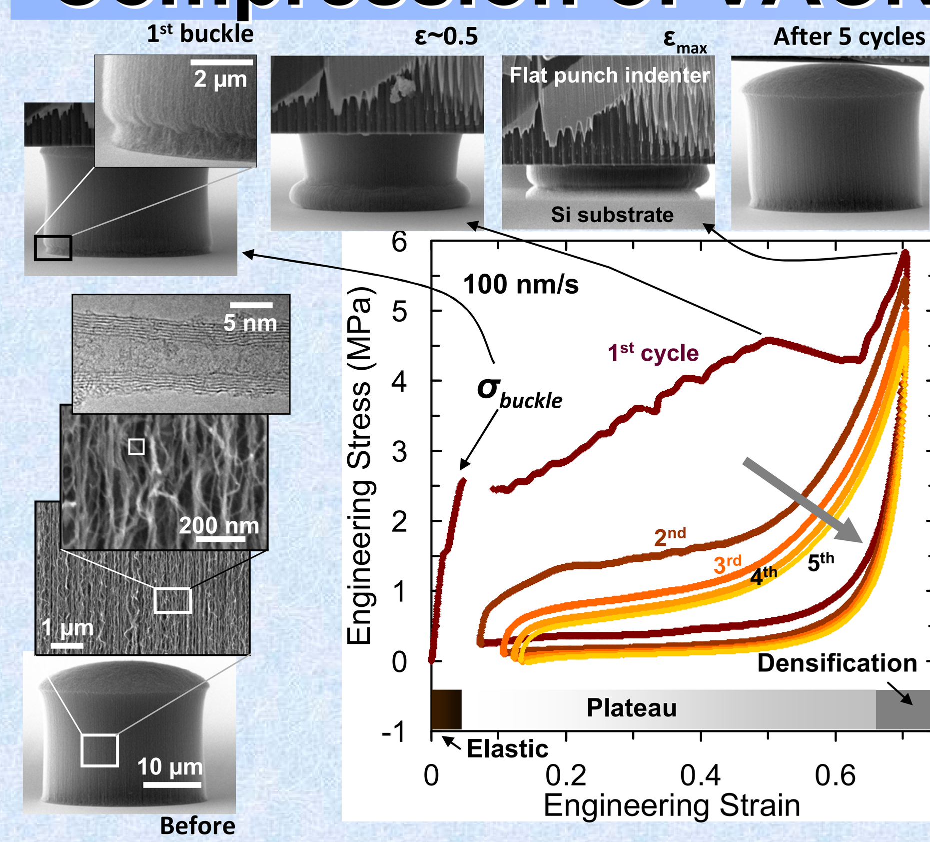
- What governs the energy absorption mechanism in VACNTs and their amazing recovery
- How do these properties change under different loading and boundary conditions in VACNTs

VACNT growth

- Photolithography - Photoresist application
  - UV Exposure
  - developing
- E-beam evaporation
  - catalyst Ti (30nm) /Al (10 nm)/Fe (3 nm)
- Photoresist removal
- CVD CNT growth - Pressure: 750 mbar
  - Temp: 750 C
  - Carbon source gas: Acetylene
- Multiwall CNT, dia 8.8±2nm, density ~80mg/cm³



Compression of VACNT micro-pillars



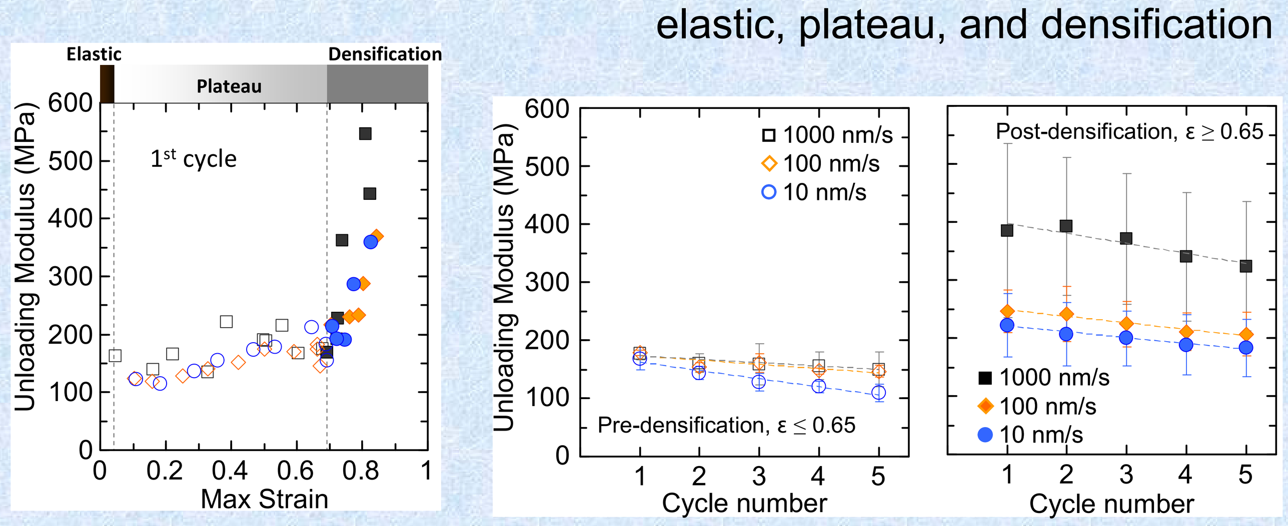
$$\sigma_{eng} = E_{unload} * \varepsilon_{eng}$$

$$\sigma_{eng} = \frac{p_{corr}}{\pi d_0^2/4}$$

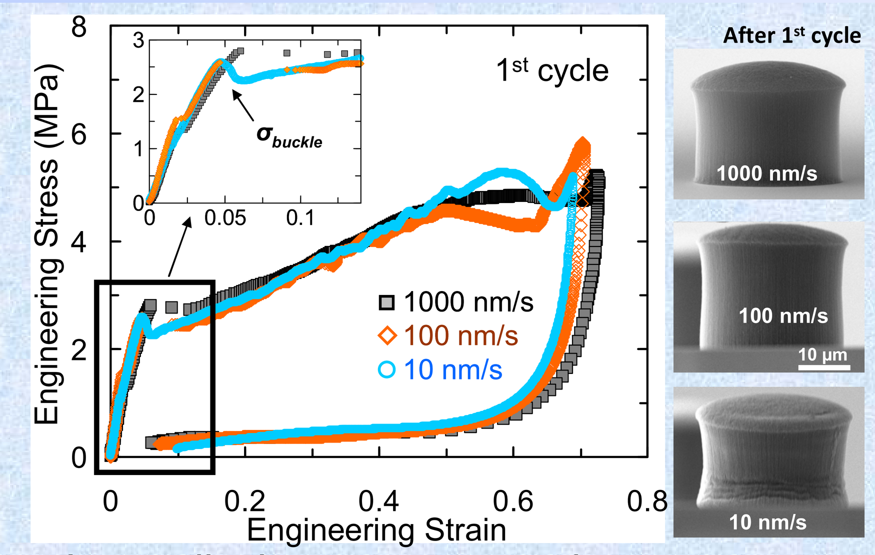
$$\varepsilon_{eng} = \frac{u_{corr}}{h_0}$$

p_{corr} - corrected load
u_{corr} - corrected displacement
h_0 - initial height of VACNT pillar
d_0 - initial dia of VACNT pillar

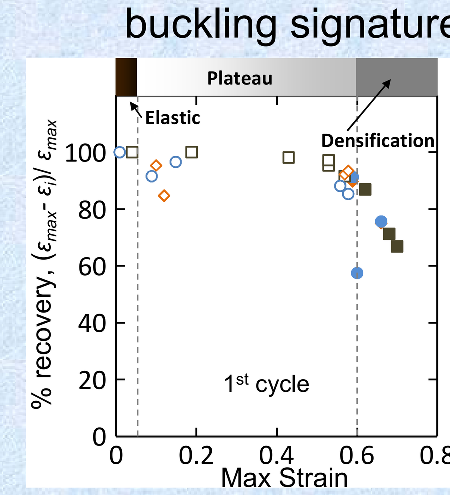
In-situ cyclic compression tests showing three distinct regimes; elastic, plateau, and densification

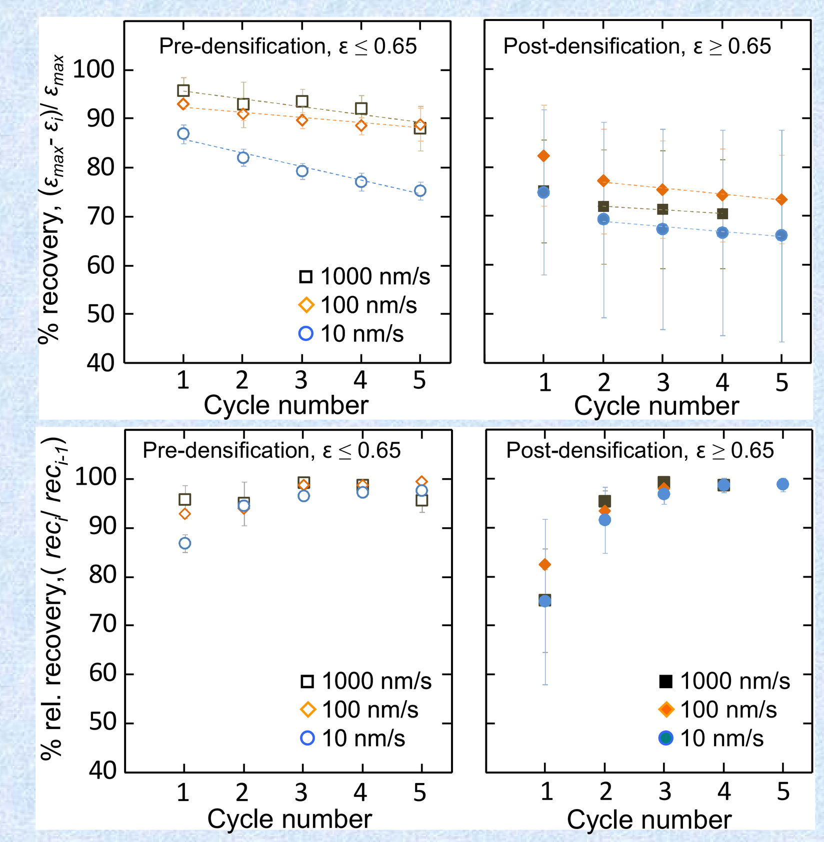


- Changes in unloading modulus at varying maximum strains show a **stiffer response at faster rates** and
- a 20-30 % drop after 5 load-unload cycles

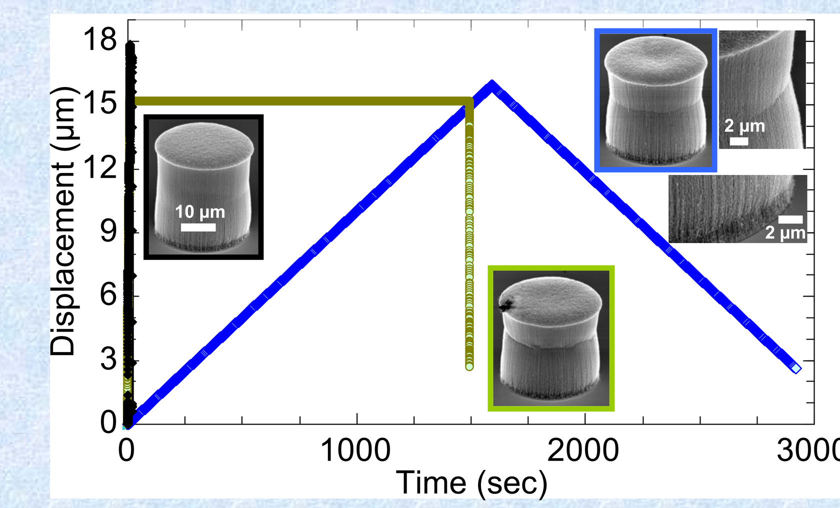


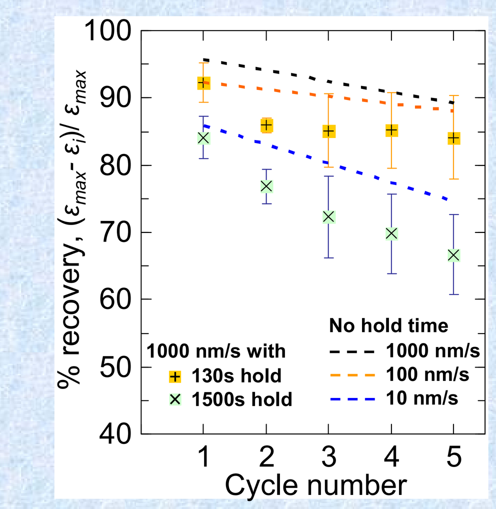
Tests at slower displacement rates show more pronounced buckling signatures and lesser recovery.



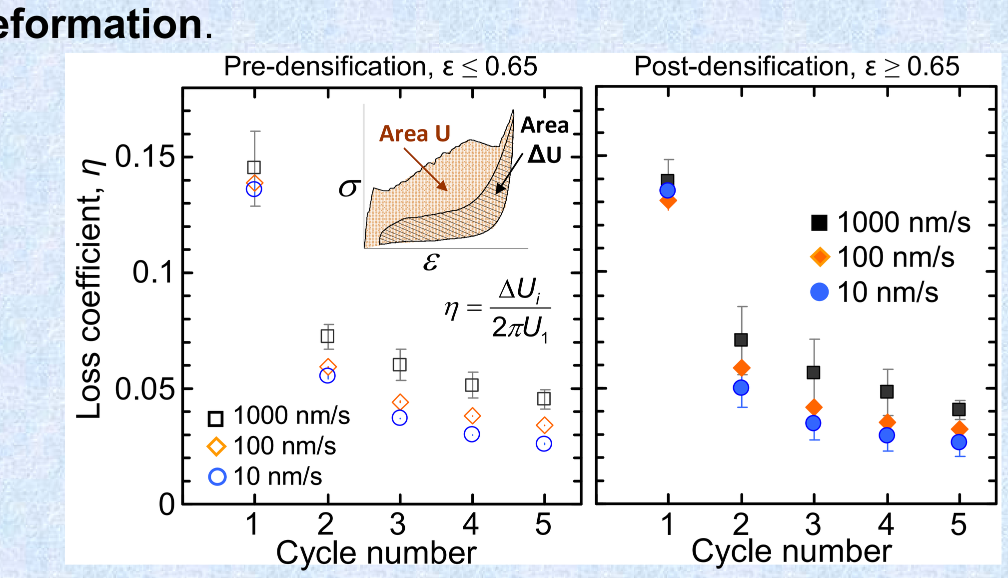


- **VACNTs show higher recovery at faster rates**
- and in the pre-densification regime. Their recoverability decreases progressively beyond densification



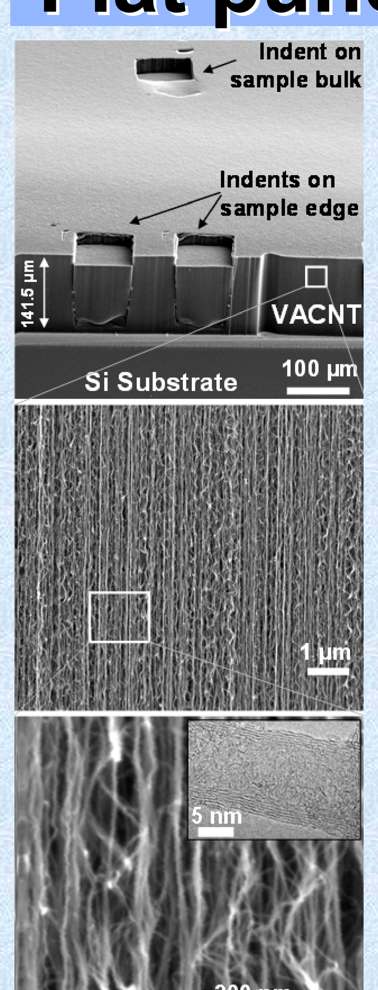


- When VACNT micro-pillars were allowed similar amounts of time for the reconfiguration to occur, they show similar % recovery.
- Thus it is the **time spent by the VACNTs under high strains**, rather than the loading history, that **determines the permanence of their deformation**.



- VACNTs show relatively high values of loss coefficient (energy dissipaption) under compression – comparable to polymeric foams.
- Similar to the trends of modulus and %recovery, the loss coefficient also increases at faster rates.

Flat punch Indentations on VACNT film



$$\sigma_{ind} = E_{eff} * \varepsilon_{ind}$$

$$\sigma_{ind} = \frac{p_{corr}}{A} = \frac{p_{corr}}{\pi a^2}$$

$$\varepsilon_{ind} = \frac{u_{corr}}{2a}$$

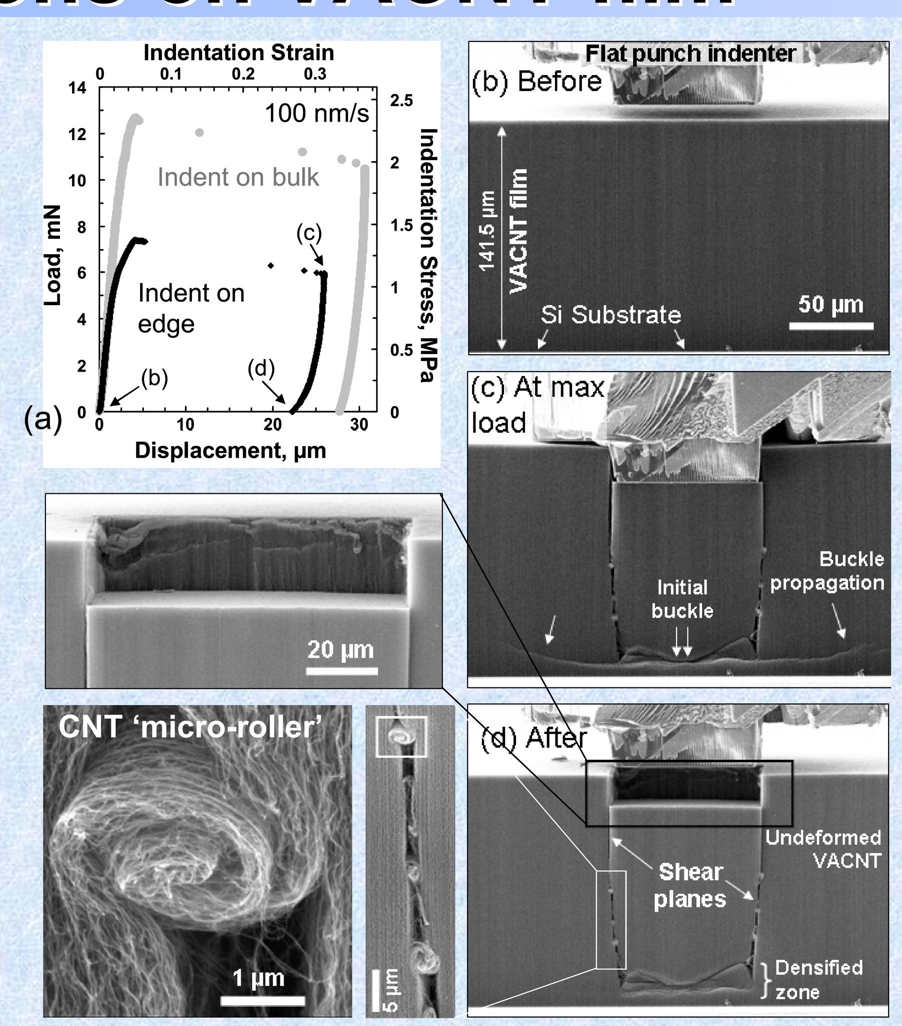
$$E_{eff} = \frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A}} = \frac{S}{2a}$$

$$\frac{1}{E_{eff}} = \frac{1-\nu_s^2}{E_s} + \frac{1-\nu_i^2}{E_i}$$

p_{corr} - corrected load
u_{corr} - corrected displacement
a - indenter radius
E_{eff} - effective modulus
S - unloading stiffness
E_s - sample modulus
E_i - indenter modulus
ν_s - Poisson's ratio sample
ν_i - Poisson's ratio indenter

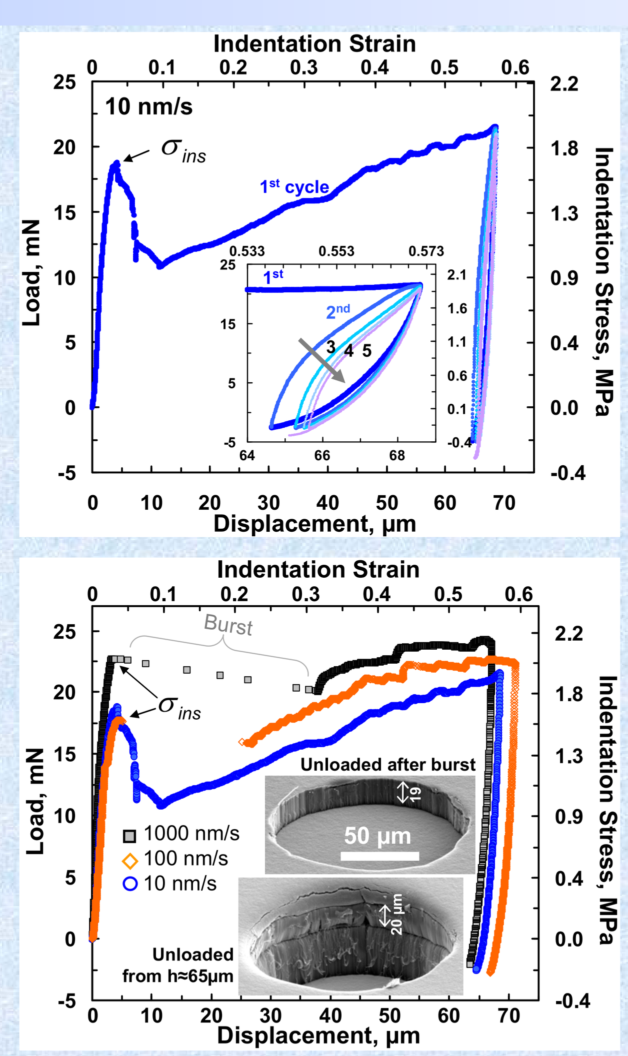
Hierarchical morphology of VACNTs:

- continuous film 260X magnification
- nominally vertical alignment of CNTs at 30,000X
- intertwined network at 240,000X
- individual multiwalled CNTs (TEM)



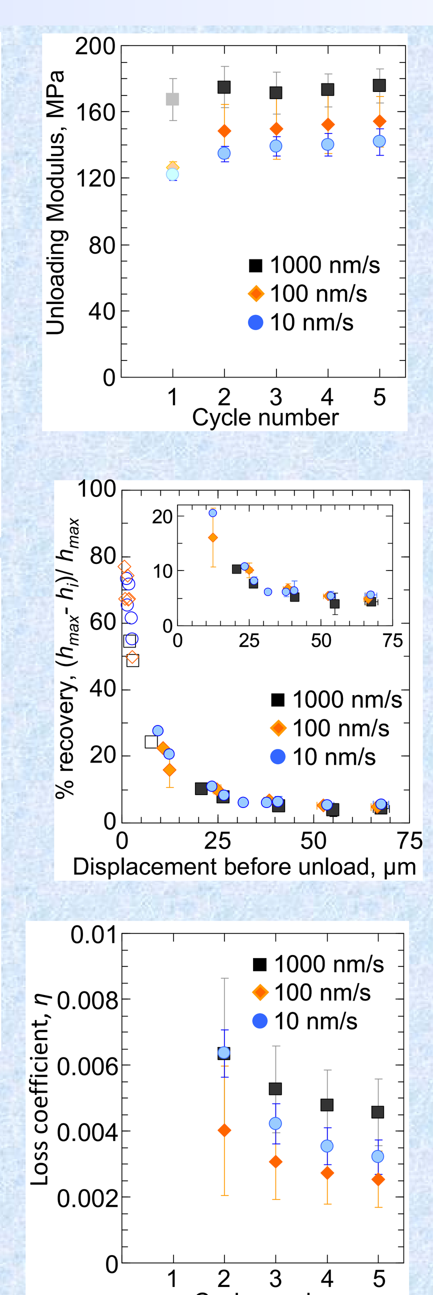
***In-situ* on-edge flat punch indentation**

- first buckle formed close to the bottom substrate
- followed by a large displacement burst ~20µm
- caused by a vertical shear in the VACNT film
- a series of tangled **CNT 'micro-rollers'** act as effective lubricants during the process

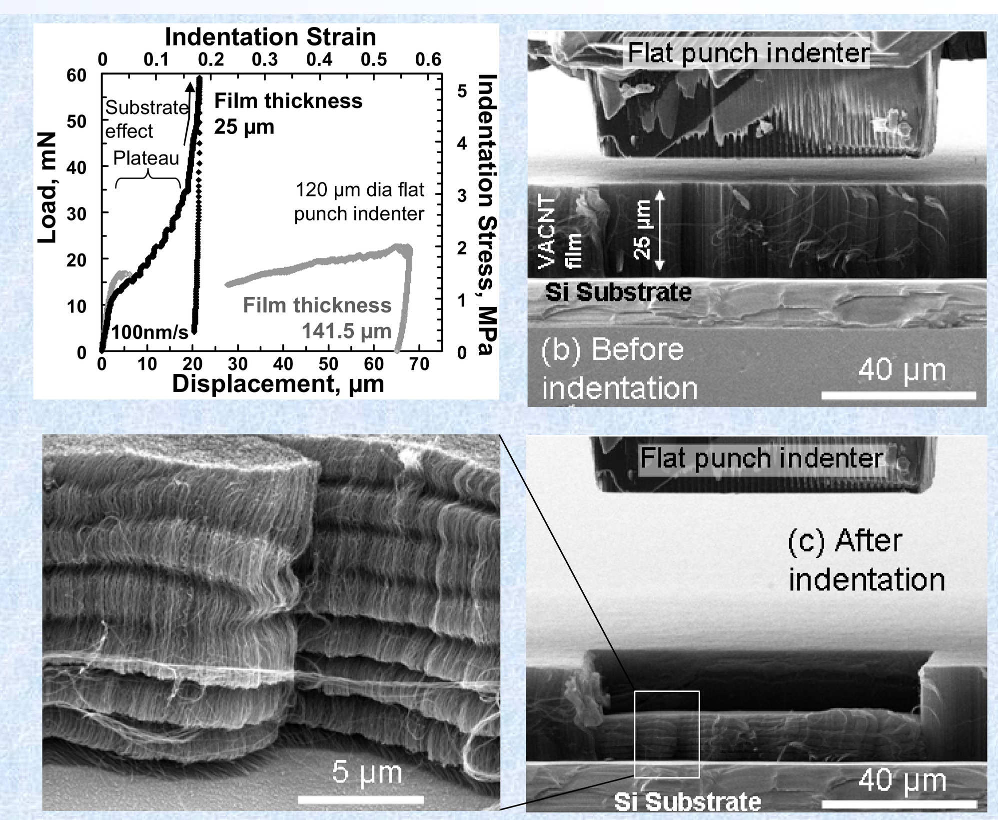


***Ex-situ* in-bulk indentation**

- three distinct regions: (i) a short elastic regime (ii) sudden displacement burst (instability), (iii) sloped plateau region.



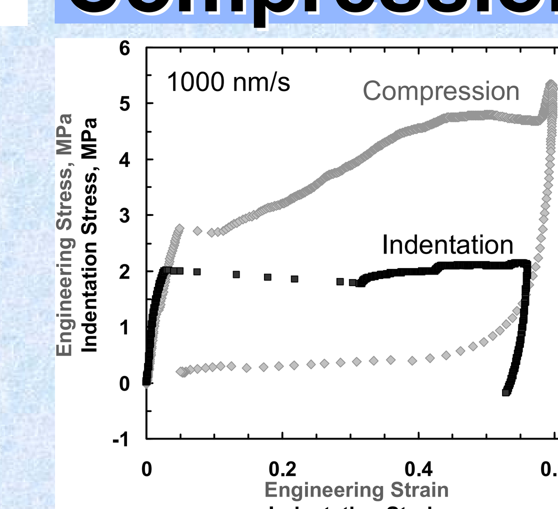
- modulus values comparable to compression
- however, the **VACNTs in indentation show very poor recovery** and loss coefficient after the burst



Effect of substrate on buckle formation

Buckle formation in the VACNT film is strongly influenced by the constraints imposed by the stiff substrate. Thus, indentations on a thin 25 µm VACNT film result in additional localized folds to continuously form along the VACNT film-height, and the indenter starts probing the folded/collapsed densified region. The stiff Si substrate in the shorter sample also causes a steeper rise in the load-displacement response in the plateau region.

Compression vs. Indentation



1000 nm/s	Indentation	Compression
Instability stress	1.75±0.3 MPa (shear)	2.69±0.1 MPa (buckling)
Recovery @ ε=0.5	4.3±0.3 %	95.7±2.8 %
Loss Coefficient @ ε=0.5	0.005±0.001	0.05±0.01
Modulus @ ε=0.5	173.7±2 MPa	176.9±11 MPa

- VACNTs show distinct modes of deformation in different boundary conditions – **shear under indentation, and buckling in compression**. During indentation the VACNT film reaches its critical shear stress before it can buckle.
- Shearing under indentation results in (<5%) recovery, compared to compression (> 95%).
- VACNT recovery in compression is strain rate dependent - **higher recovery at faster rates**
- Thus utility of VACNTs in protective applications with high energy dissipation requirements depends on the applied strain rate as well as on the loading/boundary conditions.

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