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Damage Assessment of Nanostructures

Nicola Pugno

Dept. of Structural Engineering and Geotechnics, Politecnico di Torino,

Corso Duca degli Abruzzi 24, 10129, Torino, Italy; nicola.pugno@polito.it

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Abstract. In this paper the damage assessment of nanostructures is discussed. As an example we assess the damage of nanobeams with non destructive dynamical resonance or destructive tensile tests: a small number of nanocracks, i.e., ~10, with length of ~1nm, is accordingly estimated.

Introduction

In recent years nanostructures, such as nanotubes and nanowires, have attracted great attention due to the promise of applications in sensing, material reinforcements and micro/nano-electromechanical systems. Both the mechanical resonance and the tensile testing are methods used to study the mechanical properties of nanostructures. The resonance method has been used to study the mechanical properties of one-dimensional nanostructures such as carbon nanotubes, nanowires and nanobelts [1-5]. The uniaxial tensile test is the most popular method for bulk material mechanical characterization, and it has been adapted for nanostructures such as nanotubes [5, 6] and nanowires [7, 8]. Here we present a first step towards the damage assessment of nanostructures, considering the recently investigated crystalline boron (B) nanowires (NWs) [8]. The B NWs have been synthesized with the chemical vapor deposition (CVD) method [7] and both their resonance frequency (i) and mechanical strength (ii) have experimentally been measured [8].

Shifts in the natural frequencies were observed, suggesting the possibility of the presence of nanocracks; other possible shift causes, such as intrinsic NW curvature, non-ideal clamps (often the predominant effect), spurious masses, large displacements, coating layer, etc., have been discussed elsewhere [9] and are omitted in the present analysis, with the exception of the unavoidable coating layer. A newly developed rapid electron beam induced deposition (EBID) method [10] was used to clamp the B NWs and test them in tension inside a scanning electron microscope (SEM) with a home-built nanomanipulator. Fracture strengths much lower than the theoretical material strength were observed, confirming the presence of nanocracks.

Accordingly, the resonance and tensile tests of nanobeams [8] are here discussed assuming the presence of nanocracks; non ideal/linear conditions, such as intrinsic curvature [9] or crack breathing [11-13] could also be included in the analysis. From the measured resonant frequency shifts the Gudmunson's approach [14] can in principle be applied to localize the nanocrack and quantify its depth; for multiple cracks, information on their number can also be deduced. This non destructive damage assessment can be verified by destructive tensile tests. During the tensile test the presence of a nanocrack is expected to strongly affect the failure stress. Quantized Fracture Mechanics (QFM) [15-18] (see also the related news@nature, 22 May 2006) allows one to evaluate the depth of the propagating nanocrack, also under impact loading; its position, instead, must be at the fractured cross-section: thus, in principle, nanocrack depth and position might be assessed by resonance tests and verified by tensile tests. Even if this procedure is not of simple applicability in nanoexperiments, it clearly suggests that a small number of nanocracks (~10, with length of ~1nm) was present in the nearly defect-free tested nanobeams [8], as confirmed by a comparison between nanoscale [19] versus classical Weibull Statistics [20].

Nanocrack frequency shift

Mechanical resonance can be induced in a nanowire when the frequency of the applied force (the forcing frequency) approaches the n^{th} mode proper frequency of the nanowire. According to the classical beam theory, the n^{th} natural frequency f_n of a clamped-free uniform beam, is given by:

$$f_n = \frac{\beta_n^2}{2\pi L^2}\sqrt{\frac{E_b I}{\rho A}} = \frac{\beta_n^2}{2\pi L^2}\sqrt{\frac{E_B I_B + E_O I_O}{\rho_B A_B + \rho_O A_O}}, \quad \cos\beta_n \cosh\beta_n + 1 = 0. \tag{1}$$

where E_b is the Young's modulus of the beam, I the moment of inertia of the cross-section with area A, ρ the beam density and L the beam length. The term β_n is a constant value depending on the mode (β_1=1.875, β_2=4.694, β_3=7.855 and β_4=10.996 correspond to the first four natural modes and they represent the eigenvalues of the related characteristic equation). Usually there is an oxide layer covering the nanowire surface, and thus we have to consider the second last expression in eq. (1) where the subscripts B and O denote the boron and (boron) oxide materials ($I = I_B + I_O$, $A = A_B + A_O$). Eq. (1) gives basically the definition of the "equivalent" homogeneous properties $E_b I$, ρA and allows us to determine the true boron Young's modulus E_B (by characterization of the oxide B_2O_3 layer). Thus, referring to the equivalent homogeneous structure, for a solid beam with a nearly circular cross-section of diameter D (thus the problem of coincident eigenvalues is avoided) such as the investigated boron nanowires [8], the mechanical resonant frequency can be simplified to $f_n = \frac{\beta_n^2}{8\pi}\frac{D}{L^2}\sqrt{\frac{E_b}{\rho}}$.

Assuming the presence of a nanocrack with relative depth $\zeta = a/D$ and position $r_c = x_{crack}/L$ under bending and tensile loads (x is the longitudinal coordinate), the stress-intensity factor at the tip of the nanocrack is $K_I(\zeta) = \sqrt{D}(\sigma_t g_t(\zeta) + \sigma_b g_b(\zeta))$, where σ_t is the tensile stress, $\sigma_b = MD/(2I)$ is the maximum stress due to bending moment M and $g_{b,t}$ are known shape functions [21]. The localized rotational compliance induced by the nanocrack can be evaluated as [21]:

$$C_c(\zeta) = \frac{6(1-\nu^2)D}{E_b I}\int_0^{\zeta} g_b^2(\xi)\,d\xi. \tag{2}$$

and applying the Gudmunson's perturbation method [14], the frequency shift due to the presence of the crack is predicted according to:

$$\Delta f_n^2(r_c,\zeta) = f_{n,c}^2 - f_n^2 = -\frac{\left(E_b I y_n^{//}(r_c)\right)^2}{4\pi^2 L^4} C_c(\zeta). \tag{3}$$

where $y_n^{//}(r_c)$ denotes the second derivative with respect to r of the normalized (i.e., $\rho AL\int_0^1 y_n(r) y_m(r)\,dr = \delta_{nm}$, $r = x/L$) n^{th} mode-shape for the uncracked beam, evaluated at the crack position. Thus, the ratio:

$$\frac{\Delta f_n^2}{\Delta f_m^2}(r_c) = \left(\frac{y_n^{//}(r_c)}{y_m^{//}(r_c)}\right)^2. \tag{4}$$

is only a function of the crack position r_c and should allow us, at least in principle, to localize the nanocrack by measuring two frequency shifts (e.g., related to the first (n=1) and second (m=2) vibration mode). Once r_c is known, the crack depth ζ can be estimated inverting eq. (3) from one measured frequency shift (e.g., related to the first mode, n=1).

For N cracks $\Delta f_n^2 = \sum_{i=1}^{N} \Delta f_{n,i}^2 (r_{c,i}, \zeta_i)$ and thus the depth (and position) of the "equivalent" single crack takes into account the effect of multiple cracks, giving information on their total length. Note that eq. (3) can be rewritten as:

$$\frac{\Delta E_b}{E_b}(r_c, \zeta) = \frac{E_{b,c} - E_b}{E_b} = -\frac{6(1-\nu^2)\rho A D y_n^{//2}(r_c)}{\beta_n^4} \int_0^{\zeta} g_b^2(\xi) d\xi . \quad (5)$$

For a cantilevered nanowire the normalized mode shapes are:

$$y_n(r) = \frac{1}{n_2}\left(\sin \beta_n r - \sinh \beta_n r - n_1 (\cos \beta_n r - \cosh \beta_n r)\right). \quad (6a)$$

$$n_1 = \frac{\sin \beta_n + \sinh \beta_n}{\cos \beta_n + \cosh \beta_n}, \; n_2 = \sin \beta_n - \sinh \beta_n - n_1 (\cos \beta_n - \cosh \beta_n). \quad (6b)$$

Considering the experimental results on B NWs [8] and applying the proposed methodology we present a preliminary damage assessment for the investigated nanostructures. Note that the Gudmunson's approach has no limitations in treating different crack positions (from the clamp to the free-end), see [14].

Nanocrack strength reduction

Quantized Fracture Mechanics. Analogously, the presence of a nanocrack will cause a strength reduction with respect to the ideal material strength σ_C, that can be evaluated using QFM [15-18] from:

$$\sqrt{\frac{1}{q}\int_a^{a+q} K_I^2(a) da} = K_{IC} . \quad (7)$$

where K_{IC} is the material fracture toughness and q is the fracture quantum. From eq. (7) the failure tensile stress σ_t can be predicted as:

$$\frac{\Delta \sigma_t}{\sigma_C}(\zeta) = \frac{\sigma_t - \sigma_C}{\sigma_C} = \sqrt{\frac{\int_0^{\zeta_0} g_t^2(\xi) d\xi}{\int_{\zeta}^{\zeta+\zeta_0} g_t^2(\xi) d\xi}} - 1 . \quad (8)$$

where $\zeta_0 = q/D$.

From eq. (8) the crack depth can be estimated by measuring the strength reduction ($\sigma_t - \sigma_C$), as we discuss in the following section, whereas its position can be assumed at the fractured cross-section. Note that, in contrast to the resonance test, the tensile test is influenced only by the most critical defect (i.e., with the largest stress concentration/intensification). Thus, a comparison between the two approaches could also give information on the number of defects in the nanowire.

The effect of the oxide layer on the strength measurements can be deduced observing that the total tension T to break the nanowire at the failure tensile strain ε_t is:

$$T = \sigma_t A = E_t A \varepsilon_t = (E_B A_B + E_O A_O)\varepsilon_t . \tag{9}$$

and thus the boron strength will be given by $\sigma_B = E_B \varepsilon_t$; E_t is the Young's modulus deduced by tensile tests; however note that in [8] E_B was directly measured by best fitting σ_B versus ε_t.

Nanoscale Weibull Statistics. Classical Weibull Statistics [20] assumes a large number of defects, statistically proportional to the specimen volume V (volume-defects) or to the specimen surface S (surface-defects). According to this theory, the probability of failure F for a fiber under uniaxial uniform stress σ_t and containing volume-or surface-defects is:

$$F(\sigma_t) = 1 - \exp\left[-X\left(\frac{\sigma_t}{\sigma_{0X}}\right)^{m_X}\right]. \tag{10}$$

where σ_{0X} and m_X are the Weibull's scale (with anomalous physical dimension) and shape (dimensionless) parameters and $X=V$ or $X=S$. In contrast, for nearly defect free-structures Nanoscale Weibull Statistics [19] suggests to consider X=1, and F becomes independent from the fiber volume or surface. By best fitting the experimental results on fracture strengths of B NWs with the described three different statistics, i.e., eq. (10) with $X=V,S,1$, one can statistically derive information on the defect number (small if the best fit is for X=1 or large if it is for $X=V,S$) and on their typology (volume- or surface-defects if the best fit is for $X=V$ or $X=S$ respectively). This comparison is presented in the following section.

Results and discussion

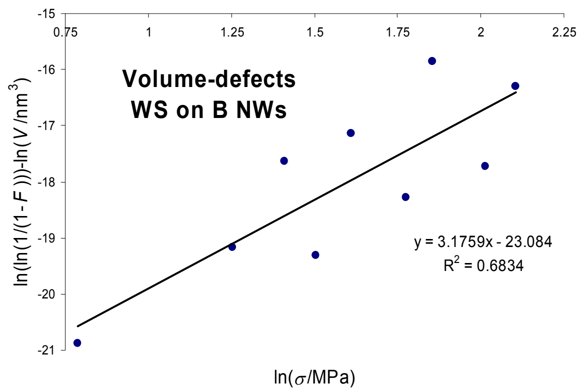
For details on the experimental tests the reader should refer to [8]. We have to emphasize that such experiments must be consider just as preliminary especially because failures always took place at the clamps. Further studies are thus required to understand the reason of this systematic failure localization (e.g., stress-concentration). In this context we simply assume that the clamping procedure was responsible for introducing localized defects. However we note that the stress-concentration imposed by the presence of a sharp clamp can formally be included in our analysis as an equivalent blunt-crack having at its tip an identical stress-concentration.

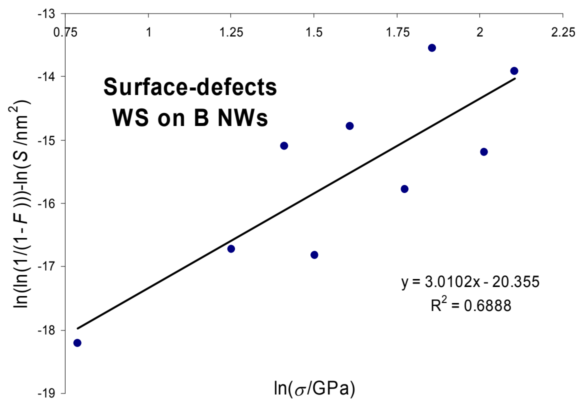
Eight B NWs were tested with the resonance method [8]. The driving frequency was swept and the resonant peaks were recorded. The amplitude-frequency responses of resonating nanowires were recorded during the experiment. The quality factors measured inside the SEM vacuum chamber (at a pressure of 10^{-6}-10^{-7} Torr) ranged between 300 and 1000. With accurate nanowire geometry and resonance frequency data, the Young's moduli of the nanowires were calculated according to eq. (1). The measured Young's moduli of these boron nanowires mostly varied between 300 to 400 GPa, as listed in Table 1. The variance in moduli in Table 1 is here interpreted as a result of the presence of nanocracks placed at the clamp, where the failures were observed, according to eq. (5). The case with the highest measured Young's modulus is assumed as defect-free. The results are reported in Table 1 and suggest an equivalent total crack length at the clamp corresponding to a significant percentage of the nanowire diameter (e.g., 50%). This total crack length is probably related to more than one smaller cracks, as suggested by the tensile tests.

Nine B NWs were tensile tested inside the SEM between two AFM cantilever tips [8]. The tensile strength of the boron nanowires was around 2-8 GPa and the maximum strain at failure was around 3%. The Young's modulus obtained from tensile testing was around 300 GPa. Table 1 also lists the tensile test results. In Table 1 the estimation of the crack length according to eq. (8) is also reported. Note that a small defect can cause a large strength reduction, due to stress-concentration/intensification. Here we have simply assumed an ideal strength of $\sigma_C \approx E_{\max}/30 \approx 12\text{GPa}$ and a fracture quantum of 0.3nm. Note the difference between the crack length results reported for dynamic resonance method, since they represent total crack lengths with those obtained from the tensile method, corresponding to the sizes of the most critical defect.

Number	Length [μm]		Diameter [nm]		Frequency [KHz]	Strength [GPa]	Young's modulus [GPa]		Crack length [nm]	
1	8.8	66.5	43	48	670.7	4.5	300	270	22	1.8
2	17.8	13.8	68	42	288.0	5.0	310	360	34	1.4
3	16.2	7.9	74	40	387.7	6.4	310	250	37	0. 8
4	35.1	44.9	77	48	93.3	5.9	370	310	24	0.9
5	20.0	7.5	52	50	163.0	4.1	300	240	27	2.3
6	13.6	45.5	48	50	303.8	7.5	270	360	28	0.5
7	6.4	25.4	80	58	2920.7	2.2	350	230	31	8.6
8	56.5	23.0	95	44	49.8	8.2	410	350	0	0.3
9		23.3		46		3.5		340		3.2

Table 1. Measurements for the 8 B NWs tested under resonance and for the 9 B NWs tested under tension. The total crack length at the clamp (where the failures took place) needed to justify the observed frequency shifts (the case with the highest measured Young's modulus is here assumed as defect-free) and the crack length of the most critical defect needed to justify the observed strength reductions (the ideal strength is assumed to be $\sigma_C \approx E_{\max}/30 \approx 12\text{GPa}$ and the fracture quantum is fixed equal to 0.3nm) are reported in the two last columns respectively.





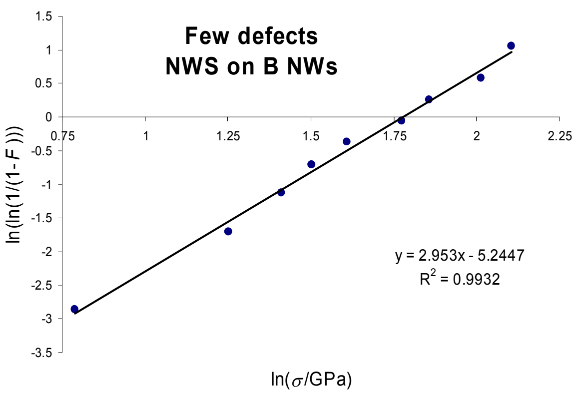


Figure 1: Classical Weibull Statistics for volume- (X=V) or surface- (X=S) defects compared with Nanoscale Weibull Statistics (X=1). The order relation between the correlation coefficients (R^2) would suggest that the tested B NWs were nearly defect-free.

These results can be rationalized assuming the presence of ~10 defects in the tested nanowires. A so small number of defects seems to be plausible also in the light of the comparison between classical versus Nanoscale Weibull Statistics, reported in Figure 1, where the experimental fracture strengths are treated assuming volume- or surface-defects, i.e., respectively by applying eq.

(10) with $X=V$ or S, or assuming a small number of defects (X=1). By comparing the coefficients of correlation for the two classical Weibull Statistics one would deduce that surface-defects prevail over their volume counterparts at the nanoscale, whereas the best interpretation (largest coefficient of correlation) is that the tested nanowires possess just a few number of defects.

Conclusions

Resonance and tensile tests of boron nanowires have been discussed in the light of a nanocrack detection. From these experimental results, based on the dynamic resonance and on the tensile test, we have deduced in each of the tested nanowire the presence of ~10 defects with a characteristic length of ~1nm. In fact, several defects are needed to justify the observed resonance frequency shifts, according to the proposed perturbation method, whereas just one of these defects is sufficient to strongly reduce the nanowire strength, as suggested by Quantized Fracture Mechanics and confirmed by Nanoscale Weibull Statistics. Obviously our nanodamage assessment has to be considered with caution, representing just a plausible scenario.

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