AIP Applied Physics Letters

How surface stresses lead to size-dependent mechanics of tensile deformation in nanowires

M. Ravi Shankar and Alexander H. King

Citation: Applied Physics Letters **90**, 141907 (2007); doi: 10.1063/1.2718487
View online: http://dx.doi.org/10.1063/1.2718487
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/90/14?ver=pdfcov
Published by the AIP Publishing

How surface stresses lead to size-dependent mechanics of tensile deformation in nanowires

M. Ravi Shankar[a)]
Department of Industrial Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261

Alexander H. King
School of Materials Engineering, Purdue University, West Lafayette, Indiana 47907

(Received 1 February 2007; accepted 24 February 2007; published online 6 April 2007)

It has been proposed that surface and interface stresses can modify the elastic behavior in nanomaterials such as nanowires. The authors show that surface stresses modify the tensile response of nanowires only when nonlinear elastic effects become important leading to cross terms between the applied stress and the surface stress. These effects are only significant when the radius of the nanowire is of the order of a few nanometers. The resulting alteration of tensile stiffness, though effected in part by the nonlinear elastic modulus, is particularly wrought by a modification of the stress state in the deformed nanowire. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2718487]

There has been great interest recently in determining the elastic behavior of nanostructured materials such as nanowires, mostly using computational models[1–6] and in a few instances, experimentally.[7,8] The fundamental interest in studying nanomaterials such as nanowires is to explore the effect of interface and surface phenomena in determining nanomaterial response. Surface and interface stresses that are generally unimportant in bulk materials gain particular importance when the surface area to volume ratio is very large, as is the case in nanomaterials.[9] A number of atomistic simulation[1–5] and computational studies[6] have been performed recently to characterize the tensile response of the nanowires. These studies have pointed to a "size-dependent" tensile elastic modulus in these nanowires.[2,5,6] While such models are helpful in characterizing the details of the nanomechanics in complex geometries with anisotropic properties, significant insights into the interplay of nanomechanical phenomena can emerge from analytic analysis to supplement these approaches. Here, we consider the effect of surface stresses on the elastic response of a nanowire within the framework of continuum elasticity. We show that the surface stresses modify the elastic mechanics of tensile deformation of nanowires on two levels. The apparent tensile stiffness in nanowires is modified in part by the interplay of nonlinear elastic effects and the large elastic strains that are direct manifestation of the surface stresses. Another modification of the tensile modulus also results from an anomalous effect of the surface stresses on the scaling of the hoop stresses in the deformed nanowire with the applied tensile load. This anomaly in hoop stress variation modifies the strain in the tensile direction through Poisson's ratio. Cumulatively, the interplay of these two effects can lead to a significant modification of the tensile modulus in nanowires that are a few nanometers in radius.

The continuum approximation is arguably not useful when the nanowire is only a few atoms thick, but for nanowires that are several tens of atoms thick, it can be a useful analytic tool to determine the role of surface stresses on the tensile response of a nanowire. In the past, similar analyses have been used to characterize the effect of surface and interface stresses on the behavior of nanostructured materials.[10–12] It has been predicted that at the nanometer length scale, the interplay of interface stresses and the nonlinear elastic behavior can lead to a supermodulus effect in thin films.[10] Direct measurements of this supermodulus effect, however, have provided moderately tenuous results.[13,14] It is noteworthy that while measurement of the supermodulus effect has been difficult, interface stresses have been measured quite effectively.[15,16]

The effect of surface stresses on the deformation of a nanowire rests on the premise that deformation work not only involves volumetric effects, a characteristic of classical solid mechanics, but also a contribution associated with surface area change. When a surface of free energy (γ) and area A is elastically deformed, the deformation work associated with this deformation dW is defined by $dW=d(\gamma A)$ such that $dW=(\gamma\delta_{ij}+\partial\gamma/\partial\varepsilon_{ij})Ad\varepsilon_{ij}$.[9] For the case of our nanowire, the effect of this surface stress f is taken to counteract the change in the area for the shaded element during tensile elongation of the nanowire, as illustrated in Fig. 1.

Utilizing the definition for the interface stresses, the work performed by surface stresses (W_i) defined on the tangent plane of the surface in terms of the surface strains is $Wi=2\pi RfL(\varepsilon_{rr}+\varepsilon_{zz})_{r=R}$. Where $(\varepsilon_{rr}+\varepsilon_{zz})_{r=R}$ denotes the

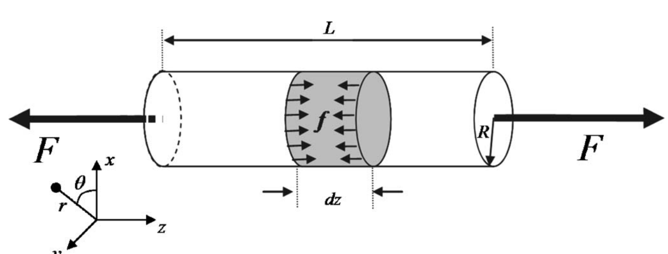

FIG. 1. Cylindrical nanowire in pure tension due to an applied force (F). Surface stresses (f) are illustrated for an element of length dz acting to contract the free surface of the nanowire.

[a)]Author to whom correspondence should be addressed; electronic mail: shankarr@engr.pitt.edu strains in the tangent plane of the surface of the deformed nanowire, R is the radius, and L is the length of the nanowire illustrated in Fig. 1.

The boundary conditions applicable to this problem of a cylindrical nanowire in pure tension are $\sigma_{rr}=0$ and $\sigma_{zz}=(F'/\pi R^2)$. We note that F' is not the same as F in Fig. 1 because the applied force (F) in the z direction is counteracted not only by σ_{zz} but also by the surface stresses. Therefore, $\sigma_{zz}\pi R^2+2\pi Rf=F$ and $F'=F-2\pi Rf$. In the immediate analysis, we only consider stresses that are linear with respect to strain. It is conceivable that when the strain values become quite large, nonlinear effects become important. We incorporate these effects in our analysis as and when necessary.

The total deformation work (U) for this problem is the sum of the classical deformation work and that due to surface stresses (W_i) such that $U=\pi r^2 L[E\nu/2(1+\nu)(1-2\nu)(\varepsilon_{rr}+\varepsilon_{\theta\theta}+\varepsilon_{zz})+E/2(1+\nu)(\varepsilon_{rr}^2+\varepsilon_{\theta\theta}^2+\varepsilon_{zz}^2)]+2\pi rfL(\varepsilon_{rr}+\varepsilon_{zz})_{r=R}$. The first two terms in this expression represent the classical deformation work[17] while the last term is the contribution from surface stresses. To a first order, we assume the nonlinearity in the elastic modulus to take the form $E=E_0(1-B(\varepsilon_{rr}+\varepsilon_{\theta\theta}+\varepsilon_{zz}))$. For long nanowires with $L \gg R$, we neglect the effect of surface stresses from the end faces of the nanowire and only consider that from the axial face of the wire. Equilibrium strain values for this problem can be determined by minimizing U with respect to strain (ε_{zz}) to show that

$$\varepsilon_{zz} = \frac{BR^2(F-2\pi fR)(-1+\nu+2\nu^2)+\pi R^4\nu E_0-\nu\sqrt{2B^2FR^4(F-2f\pi R)(1-2\nu)^2(1+\nu)+2B\pi R^6(-1+2\nu)(2f\pi R(-1+\nu)+F(1+\nu))E_0+\pi^2R^8E_0^2}}{B(-1+2\nu)\sqrt{2B^2FR^4(F-2\pi fR)(1-3\nu+4\nu^3)+2B\pi R^6(-1+2\nu)(2f\pi R(-1+\nu)+F(1+\nu))E_0+\pi^2R^8E_0^2}}. \quad (1)$$

A similar analysis can be used with $B=0$ for linear elasticity and then using variational methods it can be demonstrated that when the nonlinear effects are ignored, there are no cross terms between the interface stresses (f) and the applied force (F) because $\varepsilon_{zz}=F(1-\nu^2)/\pi R^2E-2f(1+\nu^2)/RE$. Therefore, the force versus strain curve in the linear elastic case would have the same slope, irrespective of the value of the interface stress value and thus interface stresses do not modify the elastic response.

For silica, we take $E=70$ GPa, $\nu=0.3$, $B=25$, and $f=1$ N/m, a typical value for surface stresses.[9,10,16] Clearly, when the applied force (F) is zero, the surface stresses cause a contraction of the nanowire of $R=10$ nm and this strain is -0.0031. This strain value due to the surface stresses alone is quite small even at $R=10$ nm and therefore generally insufficient to lead to any measurable change in the modulus value through nonlinear elastic effects. Therefore, the effect of interface stresses on elastic modulus of nanowires is important only when the radius is of the order of a few nanometers, say, 2 nm.

For a nonlinear elastic $R=2$ nm wire, the slope of the ε_{zz} vs F curve (l_1 in Fig. 2 $=9.6\times10^{-7}$) is greater by 38% than that predicted when nonlinear effects are ignored (l_2 in Fig. 2 $=1.3\times10^{-6}$). The slope of this curve is of course the stiffness of the nanowire expressed in newtons per tensile strain. It may be noted that the magnitude of the undeformed strain corresponding to $F=0$, due to the contracting effect of the surface stresses on the wire in the absence of the applied force, is smaller than that found when strain dependence on the modulus is ignored. This is expected because, as the nanowire contracts, its modulus increases and this makes further contraction less and less easy. Therefore, the magnitude of this strain value is smaller when nonlinear effects are considered than when they are not. It is also interesting that the interaction of nonlinear effects with interface stresses still results in a somewhat linear F vs ε_{zz} plot in Fig. 2 even for deformation strains as large as ~ 0.1 following the application of the load F. The slope of this "pseudolinear," however, response is modified by the interplay of nonlinear elasticity and interface stresses.

This reduction in slope (i.e., smaller strains for the same applied load) is only partly due to the increase in Young's modulus due to the strains for vanishing values of F contributed by surface stresses. Indeed, the increase in the value of E at a strain of ~ -0.01 for $R=2$ nm wire is only $\sim 7\%$, too small to exclusively account for the 38% increase in the tensile stiffness. The large increase in the tensile stiffness and a much-reduced tensile strain value is in good part due to the nonlinear scaling of $\sigma_{\theta\theta}$ with F. The longitudinal strain ε_{zz} is a function of both $\sigma_{zz}=(F-2\pi Rf)/\pi R^2$ and $\sigma_{\theta\theta}$ such that $\varepsilon_{zz}=(\sigma_{zz}-\nu\sigma_{\theta\theta})/E$. While E does increase, the change in $\sigma_{\theta\theta}$ during deformation is also quite influential. The inset in Fig. 2 compares the variation of $\sigma_{\theta\theta}$ with F for $R=2$ nm wire when nonlinear elastic effects and surface stresses are con-

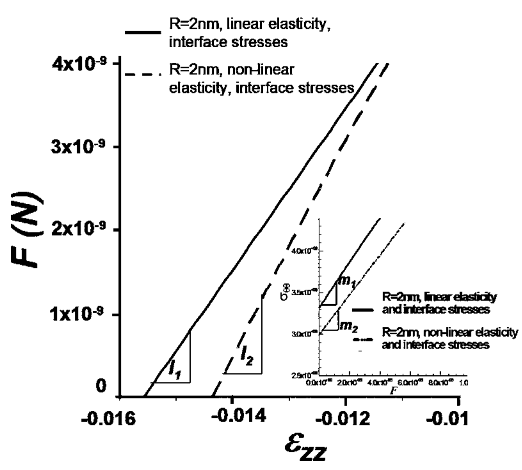

FIG. 2. Strain (ε_{zz}) vs load (F) in the elastic regime calculated for cylindrical nanowires of different radii. $l_1=9.6\times10^{-7}$ and $l_2=1.3\times10^{-6}$. Inset shows the variation of $\sigma_{\theta\theta}$ vs F wherein, slope $m_1=2.79\times10^{16}$ and $m_2=2.39\times10^{16}$.

sidered versus when nonlinearity is ignored. Not only is this tensile $\sigma_{\theta\theta}$ for the nonlinear elastic case larger but also the rate of increase in $\sigma_{\theta\theta}$ with F is much more rapid when interface stresses are considered in conjunction with nonlinear elastic effects. This rate of increase with F is almost 17% greater for the case of nonlinear elasticity (inset in Fig. 2) than when nonlinear effects are ignored. Such an anomalous increase $\sigma_{\theta\theta}$ with F would lead to a reduction in ε_{zz} as affected via the Poisson ratio and, therefore, an increased stiffness. Therefore, the origin of the supermodulus effect in this problem is not only due to the increased stiffness due to the surface stresses in the undeformed material but also to a significant extent due to the modification of the mechanics of deformation, wherein surface stresses lead to an anomalous increase in the hoop stress ($\sigma_{\theta\theta}$) of a cylindrical nanowire.

The arguments for the supermodulus effect apply without loss of generality to an "attenuated-modulus" effect if the sign of f was switched making the surface stress tensile instead of the compressive surface stress assumed in Fig. 1. When $f=-1$ N/m, we find that the tensile stiffness of the $R=2$ nm nanowire, when the nonlinear effects are considered, is $\sim$30% smaller than that for the bulk material, thus indicating an attenuated modulus. We also note that by making f negative, the resulting attenuation of stiffness is not as great as the stiffness increase when f is positive due to the asymmetric expression relating strain to F via the material elastic properties and f.

We have only considered isotropic nonlinear elasticity in our analysis. Anisotropic elastic response in crystalline nanowires may also lead to cross terms between the surface and bulk stresses, especially when the symmetry of the surface response differs from that of the bulk, and thus generate a super- or attenuated-modulus effect in much the same way that we have demonstrated here. Notably surface stresses do not generate supermodulus effects in nanowires for the case of linear isotropic elasticity.

[1] J. W. Kang and H. J. Hwang, Nanotechnology **12**, 295 (2001).
[2] H. Liang, M. Upamanyu, and H. Huang, Phys. Rev. B **71**, 241403 (2005).
[3] K. Gall, J. Diao, and M. L. Dunn, Nano Lett. **4**, 2431 (2004).
[4] M. I. Haftel and K. Gall, Phys. Rev. B **74**, 035420 (2006).
[5] J. Diao, K. Gall, and M. L. Dunn, J. Mech. Phys. Solids **52**, 1935 (2004).
[6] R. E. Miller and V. B. Shenoy, Nanotechnology **11**, 139 (2000).
[7] E. C. C. M. Silva, L. Tong, S. Yip, and K. J. Van Vliet, Small **2**, 239 (2006).
[8] H. Ni, X. Li, and H. Gao, Appl. Phys. Lett. **88**, 043108 (2006).
[9] R. C. Cammarata and K. Sieradzki, Annu. Rev. Mater. Sci. **24**, 215 (1994).
[10] R. C. Cammarata and K. Sieradzki, Phys. Rev. Lett. **62**, 2005 (1989).
[11] J. Weissmuller and J. W. Cahn, Acta Mater. **45**, 1899 (1997).
[12] J. W. Cahn and F. Larche, Acta Metall. **30**, 51 (1982).
[13] R. C. Cammarata, T. E. Schlesinger, C. Kim, S. B. Qadri, and A. S. Edelstein, Appl. Phys. Lett. **56**, 1862 (1990).
[14] H. Huang and F. Spaepen, Acta Mater. **48**, 3261 (2000).
[15] F. Spaepen, Acta Mater. **48**, 31 (2000).
[16] H. Ibach, Surf. Sci. Rep. **29**, 193 (1997).
[17] S. P. Timoshenko and J. N. Goodier, *Theory of Elasticity* (McGraw-Hill, Singapore, 1982).