

Mechanism for Nanotube Formation from Self-Bending Nanofilms Driven by Atomic-Scale Surface-Stress Imbalance

Ji Zang, Minghuang Huang, and Feng Liu*

Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112, USA

(Received 23 August 2006; published 6 April 2007)

We demonstrate, by theoretical analysis and molecular dynamics simulation, a mechanism for fabricating nanotubes by self-bending of nanofilms under intrinsic surface-stress imbalance due to surface reconstruction. A freestanding Si nanofilm may spontaneously bend itself into a nanotube without external stress load, and a bilayer SiGe nanofilm may bend into a nanotube with Ge as the inner layer, opposite of the normal bending configuration defined by misfit strain. Such rolled-up nanotubes can accommodate a high level of strain, even beyond the magnitude of lattice mismatch, greatly modifying the tube electronic and optoelectronic properties.

DOI: [10.1103/PhysRevLett.98.146102](https://doi.org/10.1103/PhysRevLett.98.146102)

PACS numbers: 81.07.De, 61.46.Fg, 68.35.-p

Mechanical bending of thin films is a ubiquitous phenomenon impacting our daily life through household thermostat to advanced microelectromechanical systems (MEMS). With the emergence of nanotechnology, the thin-film bending mechanism has been widely exploited in nanoscale devices and sensors [1–3]. Recently, another innovative use of the thin-film bending mechanism has been demonstrated for fabricating nanostructures, such as nanotubes and nanocoils, through so-called “nanomechanical architecture” of strained bilayer films [4–6].

This novel nanofabrication approach has several important technological advantages. It is completely compatible with Si technology, employing the industrial viable thin-film processing of growth, patterning, and lift-off (e.g., by etching). It is extremely versatile, applicable to most materials combinations, including semiconductors [4–6], metals [7–9], insulators [10], and polymers [11]. It also allows fabrication of different types of nanostructures, with a high level of control over their size and shape based on *a priori* theoretical designs [6].

However, there exist some fundamental limitations on the current application of the approach. So far, all the nanostructures are strictly made from bilayer or multilayer films [4–11], because misfit strain is employed as the only driving force for bending. The nanostructures, such as nanotubes, so made must have a fixed configuration with the tensile film (such as Si) as the inner layer and the compressive film (such as Ge) as the outer layer, as predefined by the lattice mismatch between the two constituting layer materials (such as Si and Ge). Here, we propose a self-bending mechanism of nanofilms that will overcome these limitations. Using theoretical analysis of surface stress and direct molecular dynamics simulations, we demonstrate that ultrathin Si and Ge nanofilms may self-bend without external stress load, under its own intrinsic surface-stress imbalance arising from surface reconstruction. This leads to self-rolled-up pure Si and Ge nanotubes, extending the nanomechanical architecture to

single films of one material, without the need for deposition of a second strained layer [6]. Under the same mechanism, SiGe bilayer nanofilms may bend toward the Ge side, opposite to what is defined by misfit strain, allowing formation of SiGe nanotubes in an unusual configuration with Ge as the inner layer. Such rolled-up nanotubes are found to accommodate very high strains, even beyond the misfit strain defined by lattice mismatch (i.e., larger than $\sim 4\%$ between Si and Ge).

Conventionally, a solid film will not bend itself without external load of “surface” stress. This is true, however, only because we have neglected the atomic details of the film structure, especially the surface atomic structure that governs the intrinsic surface stress. When the thickness is reduced to nanometer scale, the discreteness (atomic nature) of the film structure and the effect of intrinsic surface stress become increasingly prominent. This makes the bending behavior of a nanofilm not only quantitatively but also qualitatively different from that of a macroscopic thick film. Let us consider a Si(001) nanofilm of a few atomic layers in thickness. The Si(001) surface is well known to display a (2×1) -type reconstruction consisting of rows of dimers to eliminate one dangling bond per surface atom [12], as shown in Fig. 1(a). As the Si has a diamond structure, the surface dimers can orient in two orthogonal directions (rotated by 90°). For an even-layer film, the dimers on the top and bottom surface are parallel to each other, as shown in Figs. 1(b) and 1(c) for a 6-layer film; for an odd-layer film, the dimers are perpendicular to each other, as shown in Fig. 1(d) for a 5-layer film.

This odd-even alternation of surface dimer orientations will have a direct impact on the bending of Si nanofilms. The (2×1) reconstruction introduces a large surface-stress anisotropy [12]: the stress is tensile along the dimer-bond direction (σ_{\parallel}), but compressive in the orthogonal direction (σ_{\perp}). Consequently, in an even-layer film, the intrinsic stress on the top and bottom surface cancel out each other [Figs. 1(b) and 1(c)]; while in an odd-layer film,

there exists a surface-stress imbalance between its top and bottom surface [Fig. 1(d)], creating a unique *self-driving* force to bend the film.

Similarly, the atomic-scale surface-stress imbalance may *qualitatively* alter the bending behavior of SiGe bilayer films. Normally, a SiGe film bends always towards the Si side, as illustrated in Fig. 2(a), because the compressive misfit strain in the Ge layer acts as the “external” stress load to bend the whole film with the Ge tending to expand and the Si tending to contract. When the SiGe film is very thin, however, the intrinsic surface stress due to surface reconstruction will also try to bend the film. Most interestingly, surface stress will act either along or against the misfit strain in bending the bilayer film, depending on the orientation of surface dimers. This is illustrated in Figs. 2(b) and 2(c) for a [110] beam of SiGe film consisting of 3 layers of Si and 2 layers of Ge. In Fig. 2(b), the top Si surface is under tension and the bottom Ge surface under compression. Consequently, surface stress acts along misfit strain to further increase the upward bending (toward the Si side), as seen by comparing Fig. 2(a) to Fig. 2(b). However, if we switch the top and bottom surface dimer orientation as shown in Fig. 2(c), the surface stress will act against misfit strain to decrease the upward bending. To our surprise, the surface stress can be so strong that it reverses the “normal” bending direction defined by misfit strain, making the film bend downward, toward the Ge side.

The above physical analysis of surface stress induced bending of nanofilms has been confirmed by direct atomistic simulations. We have carried out extensive molecular dynamics (MD) simulations of self-bending of Si, Ge, and SiGe films that lead to formation of nanotubes, using Tersoff’s many-body potentials [13]. To simulate the bending of “one-dimensional (1D)” beams (cantilevers), we

take the beam along the [110] direction terminated with (001) top and bottom surfaces, as shown in Fig. 1(a). The system size ranges from 800 to 2400 atoms. The MD simulations were performed at the constant temperature of 50–300 K, using the 5th order predictor-corrector integration algorithm and a time step of 10^{-4} ps. We also used simulated annealing (gradually decreasing the temperature to 0 K) and static relaxation to determine the ground-state structure, with forces on all atoms converged to less than 10^{-5} eV/Å.

Both static relaxation and finite-temperature MD simulations confirmed the lowest-energy surface configuration having top and bottom surfaces (2×1) reconstructed, for beams with a thickness of at least 5 atomic layers. Below 5 atomic layers, the beam is unstable. The relative dimer orientation depends on film thickness, as illustrated in Figs. 1 and 2. All the exposed surface atoms (including sidewall surface and edge) have one dangling bond. In the MD simulations of the dynamic folding process, the atoms in the bottom surface were initially fixed and then gradually released from one end so that this end will bend upwards or downwards and eventually folds into a tube, to simulate the experimental process of releasing the film from substrate [4–11].

Figure 3(a) shows a Si nanotube formed spontaneously from self-bending a 5-layer Si(001) beam, having a radius of ~ 7.4 nm. Similar Si and Ge nanotubes have also been obtained with larger radii from thicker films. Until now, there are only a few materials can be made into nanotubes, such as carbon nanotubes by chemical vapor deposition [14]. The self-bending mechanism we demonstrate here can be, in principle, applied to make nanotubes from many different materials, as long as a surface-stress imbalance can be maneuvered. This would greatly broaden the reper-

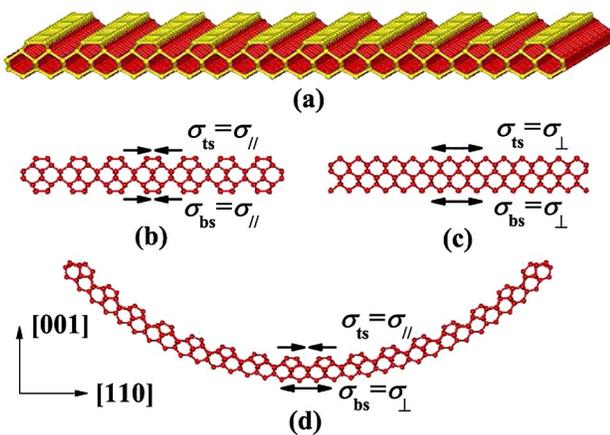


FIG. 1 (color online). (a) Illustration of Si(001)- (2×1) surface reconstruction consisting of rows of dimers. (b),(c) Side views of a 6-layer Si film, showing the parallel surface dimer orientations and the balancing surface stress on the top and bottom surface. (d) Side view of a 5-layer Si film, showing the orthogonal surface dimer orientations and surface-stress imbalance on the top and bottom surface.

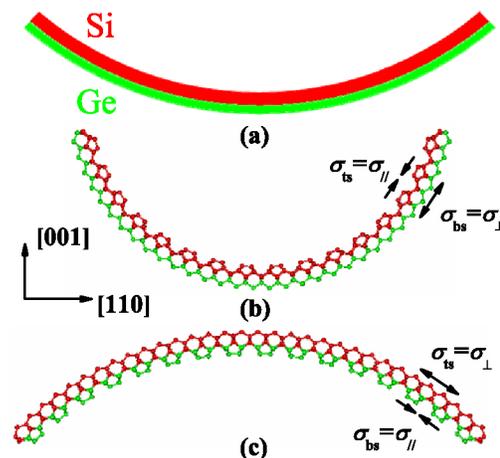


FIG. 2 (color online). (a) Conventional picture of a SiGe bilayer film that bends always toward the Si side driven by misfit strain. (b) Side view of a simulated bent SiGe film, with surface dimers arranged to have a tensile top Si surface and a compressive bottom Ge surface. (c) Same as (b) but with surface dimers and hence surface-stress configurations switched.

toire of nanotubes for both fundamental research and practical applications.

The surface stress originated self-bending mechanism can also change quantitatively and qualitatively the formation of nanotubes from strained bilayer films that has been employed currently [4–11]. Figure 3(b) shows a SiGe nanotube formed from a film of 3 layers of Si and 2 layers of Ge, in which surface dimers are orientated to have surface stress acting along the misfit film stress as in Fig. 2(b). In this case, the SiGe nanotube forms in the conventional configuration with Si as the inner layer but having a much smaller radius than what would be induced by misfit strain alone. Figure 3(c) shows another SiGe nanotube also formed from a film of 3 layers of Si and 2 layers of Ge, but having surface stress acting against the misfit film stress as in Fig. 2(c). Interestingly, this SiGe nanotube forms in a nonconventional configuration with Ge as the inner layer.

In Fig. 3(d), we show the enlarged view of folded end in Fig. 3(c), to illustrate bond formation at the interface between the folded end and the unfolded part of film. Although there are many structural defects at the interface, MD simulations show the interface to be stable; they no longer break up after sticking together. We note that the nanotubes here are tubular structures, or scrolls as made in experiments [4–11], with overlapping edges [see Fig. 3(d)] rather than a seamless tube like carbon nanotube.

Next, we analyze the radius of self-rolled-up nanotubes as a function of film thickness and quantify the magnitude of strains they may accommodate. We have simulated a series of Si, Ge, and SiGe nanotubes like those in

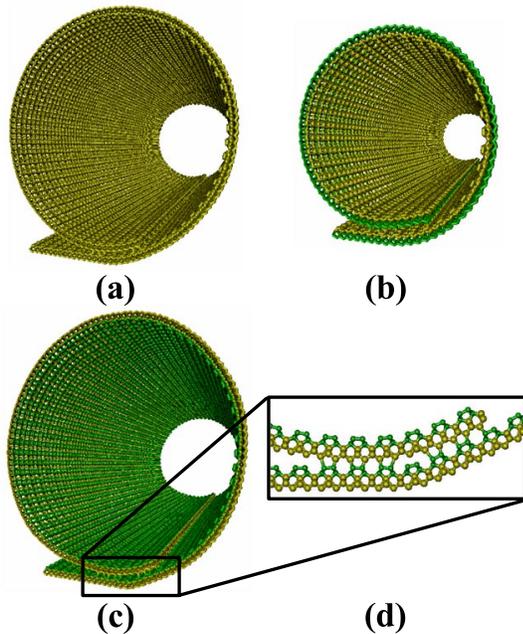


FIG. 3 (color online). MD simulated nanotubes. (a) A Si nanotube. (b) A SiGe nanotube with Si as the inner layer. (c) A SiGe nanotube with Ge as the inner layer. (d) Enlarged view of folded edge in (c).

Figs. 3(a)–3(c). In Fig. 4(a), we plot the radius of Si nanotubes as a function of thickness of odd-layer Si films ranging from 1 to 5 nm. The radius is seen to increase from 5 to 300 nm with increasing thickness. Effectively, the intrinsic surface stress arising from surface reconstruction may be viewed as the external load that drives the nanotube formation. Given the surface-stress anisotropy of Si (001) and elastic constants of Si, we might calculate the nanotube radius as a function of film thickness using the widely used Stoney formula [15], shown as the dashed line in Fig. 4(a). But its agreement with the simulation data is not good because the Stoney formula is applicable only to thick films. Instead, by accounting the effects of surface stress and strain, we have rederived a *modified* Stoney formula for calculating the radius (R) of Si nanotubes [16] as

$$\frac{1}{R} = \frac{6\Delta\sigma}{C_{\text{Si}}t^2 + 6C_{s\text{-Si}}t}, \quad (1)$$

where $\Delta\sigma$ is the surface-stress difference between the top and the bottom surface. C_{Si} is the Si film elastic constant, t

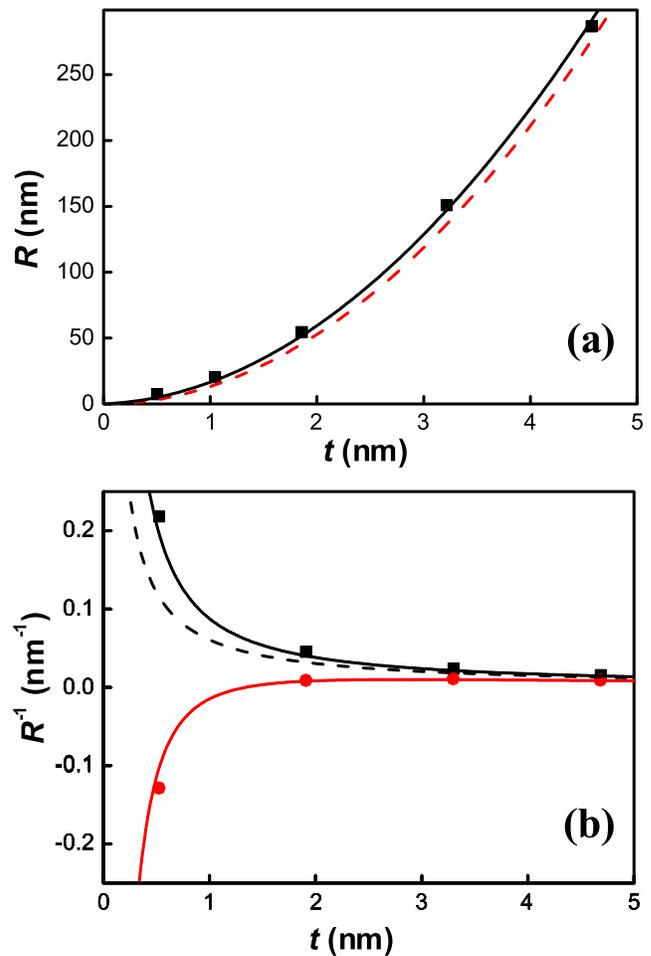


FIG. 4 (color online). (a) Radius of Si nanotube as a function of film thickness. (b) Inverse of radius of SiGe nanotubes as a function of total film thickness. Squares and circles correspond to surface configurations of Figs. 2(b) and 2(c), respectively.

is the film thickness, and C_{s-Si} is the “in-plane” elastic constant of the surface layer. Equation (1) gives an excellent fit (solid line) to the simulation data, as shown in Fig. 4(a).

In Fig. 4(b), we plot the inverse of radius (curvature) [17] as a function of total film thickness of SiGe nanotubes made from the odd-layer SiGe beams with a fixed 3-to-2 Si-to-Ge thickness ratio. There are two separate sets of data corresponding to two surface-stress configurations: one (squares) having surface stress acting along the misfit strain [Fig. 2(b)] and the other (circles) against the misfit strain [Fig. 2(c)]. Because of the presence of intrinsic surface stress, the classical Timoshenko [18] formula [dashed line in Fig. 4(b)] that accounts only for misfit strain gives a very poor description of simulated data, especially it cannot even qualitatively describe the nanotubes in the nonconventional configuration (circles). Thus, we have rederived a *modified* Timoshenko formula [16] for calculating the radius of the SiGe nanotubes, taking into account the effects of surface stress and strain. These are shown in Fig. 4(b) as solid lines, which agree very well with the simulation data.

One important question is what is the critical length scale at which the properties of nanostructures become different from their macroscopic counterparts? For SiGe nanotubes, the critical film thickness can be estimated when the “intrinsic surface stress” ($\sim 100 \text{ meV}/\text{\AA}^2$) becomes comparable to the “effective surface-stress load” induced by misfit strain that decreases with decreasing film thickness. It is about 1–2 nm when the effect of surface stress cancels out the effect of misfit strain to give rise to a zero bending curvature, i.e., a tube of infinite radius (see data of circles in Fig. 4(b)).

Because these nanotubes have a small radius of a few nanometers, they accommodate very high levels of strains which resulted from large bending curvature. Our calculations show that the in-plane tensional strain in the 5-layer Si nanotube [Fig. 3(a)] varies from a compression of -1% to a tension of $+3\%$, which is also confirmed by direct measurement of simulated bond lengths. The situation is even more interesting for a SiGe nanotube in the nonconventional configuration with Ge as the inner layer, as shown in Fig. 3(c). Normally, in a SiGe heterostructure, the strain is always lower than the nominal lattice mismatch (i.e., $\sim 4\%$) because strain relaxation makes the Ge expand and the Si contract. However, in this unusual configuration, surface stress drives the film bend towards the Ge side, making the Ge contract and the Si expand. Consequently, the Ge is compressed to a strain of -4.3% , even beyond its lattice mismatch to Si; while the Si is stretched to a large tensile strain of $+3.4\%$. Such unusually high levels of strains are expected to induce large changes in electronic properties and unusual electronic and optical responses, which may offer novel device opportunities.

Future experimental exploitation of the mechanisms we herewith demonstrate to make various nanotubes is very

appealing. InAs/GaAs bilayer nanotubes have already been fabricated with films of only a few monolayers thick [19]. It is feasible to use one layer of InAs or GaAs alone to self-bend into a nanotube by manipulating surface structure. It has also been demonstrated that ultrathin Si films can be thinned down below 10 nm on silicon-on-insulator (SOI) substrates [20], and a large single domain of $\text{Si}(2 \times 1)$ surface can be created [21,22]. Therefore, releasing of an ultrathin Si film with a single-domain top surface from SOI is possible. We note that in the actual process, the bottom surface may not be well ordered as the single-domain top surface when it is detached from the sacrificial substrate, such as consisting of mixed domains or disorder. In this case, there will still be a surface-stress imbalance between the top and bottom surface to bend the film. So, the self-bending mechanism to form “single-material” tubes continues to function, but the odd-even tenability we discussed above would be lost.

We thank the University of Utah Center for High Performance Computing for providing the computer resources used for the simulation work presented. This work was supported by the DOE.

*Electronic address: fliu@eng.utah.edu

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