

Nanomechanical Architecture of Strained Bi-layer Thin Films: from design principles to experimental fabrication**

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Nanofabrication and synthesis has become one of the most active research areas in recent years. Certain class of nanostructures have been successfully fabricated in bulk or grown on surfaces by self-assembly and self-organization process^[1-3] and sometimes combined with lithographic patterning^[4]. However, very often the nanostructures are made in an empirical manner lacking a sufficient level of control. Despite the enormous success we have so far enjoyed, such as with carbon nanotubes^[1,5] and Zinc-oxide nanobelts,^[2] nanofabrication and synthesis with most materials are still very difficult. There exists a strong need for the development of nanofabrication techniques with a higher degree of control on size and geometry as well as with a high degree of versatility applicable to different materials. Here, we demonstrate the generic design principles of an emerging nanofabrication approach based on *nanomechanical architecture* of strained bi-layer thin films. It allows fabrication of a variety of nanostructures, such as nanotubes, nanorings, nanodrills, and nanocoils, using combinations of different materials with an unprecedented level of control.

Like a bimetallic strip in a thermostat that bends due to different thermal stress in the two metal strips, a strained bi-layer thin film bends due to lattice-misfit strain in the two layers. In particular, when the film thickness is reduced to the nanometer scale, its bending magnitude can be so large that it can fold into tubular shapes with multiple rotations as the film length becomes longer than $2\pi R_0$, where R_0 is the characteristic radius of the film bending curvature. Remarkably, this simple bending phenomenon has recently been exploited for fabricating a variety of nanostructures, ranging from nanotubes,^[6-10] nanorings,^[11-13] nanodrills (see Fig. 1b), nanocoils,^[6,14] (see Fig. 1c) nanorods,^[12] to nanomirrors.^[15,16] Figure 1 shows examples of an array of nanorings (Fig. 1a), a nanodrill (Fig. 1b) and a nanocoil (Fig. 1c), all formed from strained Si/SiGe bi-layer films.^[17]

All these different classes of nanostructures are formed by the “same” mechanism – namely the tendency of strained bi-layer films to bend (or to fold). We therefore name them the “**nanomechanical architectures**” of strained bi-layer thin

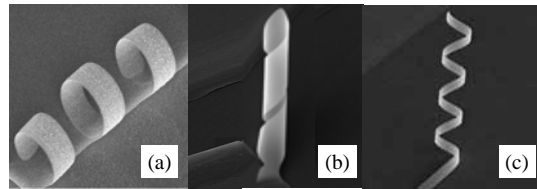


Figure 1. SEM image of nanoarchitectures fabricated from strained Si/SiGe bi-layer films. (a) Nanorings with a thickness of 80 nm, radius of $\sim 3.0 \mu\text{m}$, and width of 3 μm ; (b) nanodrill with a thickness of 110 nm, radius of $\sim 2.4 \mu\text{m}$, and width of 10 μm ; and (c) nanocoil with a thickness of 110 nm, radius of $\sim 2.4 \mu\text{m}$, and width of 2 μm . In general, we can vary the thickness from 10 nm to 200 nm and dimensions from 20 nm to 100 μm .

films. One outstanding advantage of this nanofabrication technique is its versatility. Not only can a variety of “nanomechanical architectural designs” be made, but they can also be made with different materials, including semiconductors, metals, and insulators, as well as combinations of these materials. Furthermore, a high degree of control should be, in principle, achievable. Not only different nanoarchitectures can be designed, but also their size and shape can be tuned over a wide range by choosing different combinations of materials, varying film dimensions, and applying external forces. This approach also makes it possible for parallel mass production of identical or different nanostructures.

The promising potential shown by this novel and fascinating approach has attracted a lot of recent interests.^[6-16] However, the work to date remains largely empirical; most structures are made in a trial-&-error manner. This is due mainly to the lack of complete understanding of the underlying physical principles, which hinders a higher degree of experimental control. Here, we theoretically analyze and experimentally demonstrate fundamental mechanisms governing the nanomechanical architecture of strained bi-layer nanometer-thick thin films. We establish certain generic “design principles”, which will lead to selective fabrication of different classes of nanostructures, such as nanotubes and nanorings vs. nanodrills and nanocoils, in a controllable manner. Our analysis will be based on continuum mechanics theory for systems that the atomic structures and surface/interface effects are not yet important.

Certain well-defined and universal physical conditions and geometric relationships exist controlling the size of the same class of nanostructures as well as the formation of different classes of nanostructures. One design principle underlying the formation of nanotubes lies in the control of their radius. The tube radius can be *a priori* designed because it equals, in principle, to the radius of bending curvature of the given strained bi-layer film. This principle has been applied by Deneke *et al.* in fabricating a series of InGaAs/GaAs nanotubes with a radius ranging from 10 to 300 nm.^[8] Our further analysis shows that actually there exists a maximum bending curvature for a given set of film thickness combinations, which sets a theoretical limit on the smallest nanotube one can produce. It will be interesting for future experiments to confirm such limit.

The design principles for fabricating different classes of nanostructures are more complex. Let’s analyze the principles governing the formation of nanotubes/nanorings

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vs. nanodrills/nanocoils in terms of the bi-layer film geometric and elastic properties. Qualitatively, one can expect that the film is more likely to fold into a nanotube or nanoring if the film width is large, while it may fold into a nanodril or nanocoil only if the width is small. Thus, there must exist a design principle in terms of the film width, and more generally in terms of the film dimensions, which separates the formation of a nanotube from a nanocoil.

To illustrate this point, we examine the relative stability of a nanotube vs. a nanocoil for given film dimensions of length L , width W and thickness t , as shown in Fig. 2. The characteristic bending curvature of a strained bi-layer film depends on misfit strain (ε) and the thickness and elastic constants of the two constituting layers. If we assume, for simplicity, the two layers has the same thickness ($t/2$) and elastic constants, the characteristic curvature can be calculated as $K = -(3\varepsilon)/(2t)$.^[18-21] Then, the film will fold into a tube or coil whose rotations having a characteristic radius $R_0 = 1/K$ and a perimeter length $L_0 = 2\pi R_0$.

Whether the film will fold into a tube or coil is uniquely controlled by some intrinsic relations between the film geometric dimensions (e.g., the width W) and its characteristic bending scales (e.g., L_0). First, let's consider the film to be elastically isotropic, then it may fold along any direction with equal bending energy. In this case, a coil can always be energetically favored to form over a tube when $W < L_0$. This is because the film can always fold into a coil

by choosing a folding direction having an angle, θ with its long edge larger than $\theta_c = \sin^{-1}(W/L_0)$, as shown in Fig.

2, so that all the rotations in the coil adopt the optimal radius R_0 with the minimum bending energy. In contrast, if the film folds into a tube with multiple rotations by folding along a direction having an angle with its long edge small than θ_c , only its first rotation can adopt R_0 , while additional rotations must adopt a radius larger than R_0 with extra cost of bending energy. Therefore, there exist two critical geometric conditions for coil formation, i.e., $W < L_0$, and $\theta > \theta_c$. The spiral angle of the coil depends on the folding direction as $\alpha = \tan^{-1}(d/R_0)$ ($d \geq w$), as shown in Fig. 2, and the minimum allowed spiral angle for any coil is $\theta = \tan^{-1}(W/R_0)$. If W and L are comparable, both larger than L_0 , the film may fold randomly along any direction, as we have observed in experiments.^[22]

Next, we consider the film to be elastically anisotropic. In this case, the film is energetically preferred to *only* fold along the elastically most compliant direction. This adds another variable in the design principle for formation of nanotube vs. nanocoil, which now depends critically on the alignment between the most compliant direction and the film long edge. If the most compliant direction forms an angle with the film long edge larger than θ_c , then the film folds naturally along

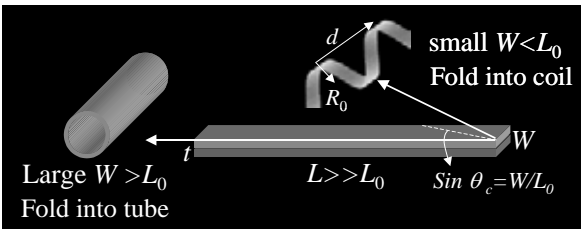


Figure 2. Schematic illustration of a strained bi-layer film folding into a nanotube when its width W is large, but into a coil when its width W is small. The arrows indicate the folding direction.

its most compliant direction into a coil as discussed above; otherwise, the film folds naturally into a tube.

Now, we demonstrate controlled experimental fabrication of nanorings vs. nanocoils, to validate the design principle based on elastic anisotropy, as also shown before.^[6,15] We use ultrathin Si/SiGe bi-layer films as a model system, which are grown by molecular beam epitaxy (MBE) and chemical vapor deposition (CVD) onto a sacrificial SiGe on Insulator (SGOI) or SOI substrate. Based on elastic anisotropy of Si and Ge, we pattern the thin films into cantilevers of two different orientations: one along the (100) direction (Fig.3, upper left), i.e., the most compliant direction of Si and Ge; the other along the (110) direction (Fig. 3, upper right). The cantilevers are then released by etching, which will bend upward and fold into nanorings or nanocoils.

As *a priori* designed, Figure 3 (left panel) shows that the (100)-orientated cantilevers fold naturally along the most

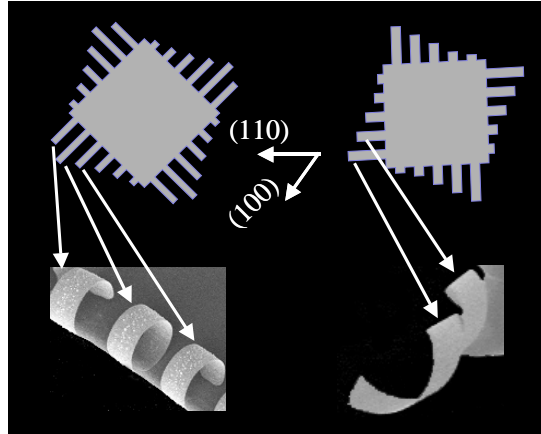


Figure 3. Experimental demonstration of strained Si/SiGe bi-layer cantilevers folding into nanorings when they are patterned along (100) direction, but into nanocoils when they are patterned along (110) direction, as they prefer to fold along the most compliant (100) direction. The nanorings have a thickness of 60 nm, radius of $\sim 3.2 \mu\text{m}$, and width of $3 \mu\text{m}$; the nanocoils have a thickness of 76 nm, radius of $\sim 2.8 \mu\text{m}$, and width of $4 \mu\text{m}$.

compliant (100) direction into nanorings. All three cantilevers fold with the same characteristic radius, with the longest cantilever ($20 \mu\text{m}$) forming a complete ring and the two shorter cantilevers ($15 \mu\text{m}$) forming a partial ring. In contrast, the two longest (110)-orientated cantilevers fold into nanocoils (Fig. 3, right panel), because the film tends to fold along the most compliant (100) direction. The radius of nanocoils ($\sim 2.8 \mu\text{m}$) is slightly smaller than that of nanorings ($\sim 3.2 \mu\text{m}$), because the characteristic bending radius of the (110) cantilever is smaller than that of the (100) cantilever for the given thickness ratio, also consistent with theory.

So far, we have considered the film to fold naturally with only the bending distortion. In addition, the film may fold also with shear distortion under external forces, in particular to form a coil. Then, the scenario for tube formation vs. coil formation becomes much more complex. Let's consider a particular case when the film is most compliant in the direction along its long edge so that without shearing it will naturally fold into a tube, as discussed above. Apparently, only the first rotation has the optimal radius of bending with the minimized bending energy, while others have too large a radius. Thus, the nanotube forms with an energy penalty of bending.

Alternatively, one may pull the nanotube along its axial direction into a coil by an external force (e.g., using an AFM tip), so the film effectively folds into a nanocoil by bending plus shearing. In this case, all the rotations can adopt the same optimal radius of bending, R_0 , but each rotation is sheared relative to its neighboring rotations by a minimum shear strain of $\pm W/L_0$. Consequently, the bending energy in the nanocoil is minimized in all the rotations, but at an extra energy cost due to shearing. Thus, the nanocoil forms with an energy penalty of shearing.

We have calculated the total energy of a nanotube vs. a nanocoil, as a function of the film length L , width W , and thickness t . For the nanotube, the first rotation has a radius of R_0 , and the n -th rotation has a radius of $R_0 + (n-1)t$. A film of total length, L , will fold into a nanotube of N rotations, with

$$L = \sum_{n=1}^N 2\pi[R_0 + (n-1)t] \quad (1)$$

Assuming the two layers has the same thickness and elastic constants, the bending energy in the first rotation can be analytically solved as

$$E_b = \frac{1}{32} M_b \varepsilon^2 (L_0 W t) \quad (2)$$

while the total energy needs to be numerically calculated by summing over bending energy in all N rotations. For the nanocoil, its total energy consists of both bending and shearing energy. They are the same in all rotations and can be calculated analytically as

$$E = \frac{1}{32} M_b \varepsilon^2 (L W t) + \frac{1}{2} M_s \gamma^2 (L W t) \quad (3)$$

where M_b and M_s are respectively bending modulus (along the most compliant direction) and shearing modulus, and $\gamma = d/L_0 \geq W/L_0$ is the shear strain associated with coiling (see Fig. 2).

Figure 4 shows the calculated “phase diagram” for a 60 nm thick Si/Ge bi-layer film, defining the geometric regimes for nanotube vs. nanocoil. For a given film length, there exists a critical film width, above which the nanotube forms and

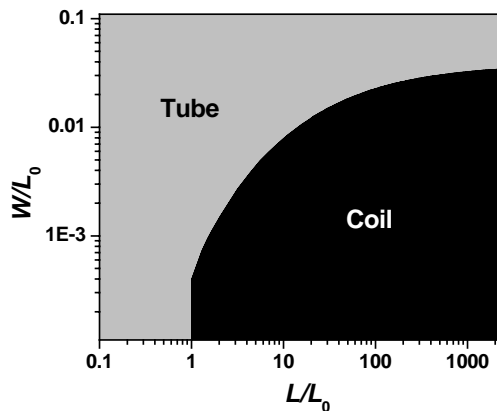


Figure 4. Log-log plot of phase diagram of nanotube and nanocoil, as a function of reduced film length L/L_0 and reduced width W/L_0 .

below which the nanocoil forms. Conversely, for a given film width, there exists a critical film length. The minimum length

for coil formation is L_0 . There exists an “upper” limit of film width for nanocoil formation, above which only nanotube forms. The maximum width for coil formation is only about 3% of L_0 , indicating that nanocoil is generally much harder to form by shearing when the most compliant direction is aligned with the long edge of the film.

The above phase diagram defines the thermodynamic limit for nanotube vs. nanocoil, in terms of film length and width. In reality, external force is needed to transform the naturally folded tube (kinetically limited) into more stable coiling state. In addition to film dimensions, the phase diagram depends also on film elastic properties. For example, the phase boundary line in Fig. 4 will shift upward with either decreasing shear modulus or increasing bending modulus. More generally, the coiling condition depends on the angle made between the most-compliant direction and the film long edge.

Besides the *intrinsic* geometric and physical conditions, the nanomechanical architecture of strained bi-layer films depends also on *extrinsic* processing parameters. One important processing parameter is etching rate, because the final bent structure depends on the rate of strain relaxation (i.e., the rate of stress waves) relative to the etching rate (i.e., the rate film being released from the sacrificial substrate). Both our computer simulations and experiments^[22] show that the free-up film must have long enough relaxation time to roll into a tube requiring the etching rate to be sufficiently slow. If the etching rate is too fast, the film may peel off the substrate into ripples instead of rolling into a tube. It is also possible to release the film from both ends to form a pair of same nanostructures^[23] or new types of nanostructures. We have been applying computer simulations as an effective tool to test the theoretical design principles and to explore novel nano-objects.

In summary, we demonstrate by both theory and experiment some generic design principles for a novel nanofabrication approach, the nanomechanical architecture of strained bi-layer films, in terms of geometric, physical and processing parameters. Our theoretical analyses show that there exist fundamental geometric and physical conditions controlling the formation of nanotube (nanoring) vs. nanocoil (nanodrill). For an elastically isotropic film, the critical geometric condition for nanocoil formation is that the film width (W) must be smaller than $L_0=2\pi R_0$, where R_0 is the characteristic bending radius of the given bi-layer film. For an anisotropic film, nanocoil formation depends critically on the alignment of the most compliant direction of the film with respect to the film geometry (i.e., its long edge). We experimentally validate these design principles by fabrication of nanorings, nanocoils and nanodrills, using advanced growth, patterning, and etching techniques. Furthermore, we construct the theoretical phase diagram for nanocoil formation with additional shear distortion under external forces.

We believe the nanomechanical architecture of strained bi-layer thin films will become one of the most viable nanofabrication techniques in the future, because of its unparallel versatility in making a variety of different nanostructures from combination of different classes of materials and its unprecedented level of control allowing fabrication of nanostructures with *a priori* designs. Our study not only contributes to the advancement of this emerging nanofabrication approach, but also has important implications on other existing approaches, especially for fabrication and synthesis of various nanotubes, nanobelts and nanorings.

Experimental

All the bi-layer films were grown by deposition of Si onto a SiGe strained layer on insulator (SGOI) using solid source

molecular beam epitaxy (MBE), except the one shown in the Fig. 3 (lower right) that was prepared by ultra high vacuum chemical vapor deposition (UHV-CVD) growth of Si/SiGe bi-layer onto SOI. Both MBE and CVD SiGe film have a concentration of ~20% Ge. The thickness of CVD film are ~30nm Si/~36nm SiGe, determined by x-ray diffraction. For MBE film, we are able to grow five different thickness (20, 40, 50, 70, and 100nm) of Si layer *in situ* onto a single piece of SGOI substrate by rotating a shutter in MBE chamber, allowing the film to fold with different characteristic bending radius. The growth rate is 0.55 Å/second at substrate temperature of 585 C°, measured by an optical pyrometer. The MBE/CVD growth of Si layer was monitored with reflection high-energy electron diffraction, which showed clearly a (2x1) reconstruction pattern on sample surface during the entire growth.

The SGOI substrate is a free sample from SOITEC. The thickness and composition of SGOI are about 44nm Si with 20% Ge on 190nm SiO₂. The sample was cleaned with 10% hydrofluoric (HF) acid to etch off the native oxide grown in air on original SGOI surface, followed with 10 minutes piranha clean (H₂SO₄/ H₂O₂), and few seconds 10% HF etching to remove the oxide layer produced during piranha clean. For UHV-CVD growth, we added an additional 15 minutes SC1 clean (NH₄OH/H₂O₂/H₂O-mixture) at ~80 °C and dipped deliberately the sample with diluted HF acid to terminate the surface with hydrogen (H) before loading it into the CVD chamber, in order to prevent the growth of native oxide in air.

We performed photo and electron-beam (E-B) lithography to pattern the thin films into cantilevers. Basically, an array of cantilevers with different dimensions and orientations was created on each side of a 50x50 μm square, as shown in Fig. 3. The common width of the (100) cantilever is 3μm and the length varies from the longest to the shortest from 20, 15, 10, 6, to 3 μm. The spacing in between is 5μm. The width of the (110) cantilever is 6μm and the length from 36, 26, 16, 6, to 4 μm. The spacing in between is 2 μm.

After lithography, the desired patterns were transferred onto the Si/Si_{0.8}Ge_{0.2} bi-layer film by using O₂ + SF₆ reactive ion etching. The underlying sacrificial oxide layer was selectively etched off by the vapor of HF acid to release the cantilever, which bended upward and folded into nanorings or nanocoils. The vapor HF releasing process was carried out at temperature of 40 C° with a time duration of 30~60 minutes. The most important advantage of this technique is that it is a single process without subsequent rinsing steps to avoid the released structure sticking onto the substrate. Also, for this purpose, it is necessary to create a strain configuration with Si film grown on top of SiGe by using the unique SGOI wafer. In the normal configuration with SiGe film grown on top of Si by using the conventional SOI wafer, the released bi-layer film would bend downward and being blocked to fold completely.

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