Strain Engineered Silicon Nanomembranes

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Introduction
The idea that extremely thin single-crystal semiconductor films could be fabricated usefully is only a few years old [1]. The wider recognition that such structures represent a potential new class of nanomaterial with unique nanoscale properties is even more recent [2, 3]. The fact that this class of nanomaterial can include not just semiconductors is only beginning to be appreciated. Giving impetus to the nanomembrane field has been the visual impact of structures, such as tubes, coils, and ribbons, that involve the use of lattice strain and unbalancing this strain using two (or more) compositionally different but pseudomorphically grown layers. [1, 3, 4] The fabrication of free-standing, free-floating, or transferred semiconductor membranes does not have to involve strain [5, 6], and even when it does, flat 2D structures can also be made if the strain is properly balanced [7], suggesting that integration with the essentially flat world of current semiconductor and ferroic and ferroelectronic devices is highly feasible.

The primary materials used for nanomembrane creation are Group IV-based (Si and Ge), for several reasons. The principal one is the ubiquity of silicon-on-insulator (SOI), now quite commonly used in the semiconductor device industry. In SOI a SiO₂ layer is interspersed between a crystalline top Si layer (the template or device layer) and the bottom Si (handle) wafer. The ability to etch the oxide very selectively makes it simple to remove the top Si layer as a membrane. Additionally the Si template layer can be very precisely thinned by repeated slow oxidation and oxide etching, so that template layers from 100s of nanometers to as a few as several nanometers are possible.

Where's the nano?
"This is just thin silicon, we know all about silicon. Where is the ‘Nano’?" The occasional expression of dubious bemusement suggests the thought “Yes, nice little structures, but what could possibly be interesting, say, in comparison to carbon nanotubes or semiconductor nanowires?” The thought is not entirely without merit: some of the most immediate impact of Si nanomembranes does not involve new nanoscience or nanotechnology; for example, very-high-speed flexible electronics with transferred Si or strained-Si membranes [5, 8] (“Supersmart Saran Wrap” [9]). Yet without resorting to the usual polemics of what constitutes nano (iPod Nano™, Nano fish products, Nano hair care, Nano golf gifts and equipment,…), one can point to unique features that are related to thinness, even in a sheet of pure Si. This article focuses on illuminating several such features in Si and strained Si/SiGe systems.

Fabrication
Apart from the idea that one can literally create sheets of single crystal not more that 30 to 50 atomic layers thick, in lateral sizes that correspond in aspect ratio to a bed-size sheet of single-strength aluminum foil, by releasing them from a selectively etchable substrate, and transfer them to other hosts, what distinguishes nanomembranes is strain without the usual extended defects. This strain can be introduced using heteroepitaxial growth techniques that have been extremely well developed over the last 50 years. A lattice mismatched film can be grown pseudomorphically on a single crystal up to a thickness that does not exceed the kinetic critical thickness for dislocation formation, or more usually, the thickness at which 3D islands start to form. Additional layers can be grown as long as
these conditions are met. The growth process, as well as release and membrane formation, has been described in detail. [7, 10] By releasing the strained-layer structure (at least one of the layers is strained before release), the strain in the initially strained layer is elastically shared among all layers, the initially strained layer relaxing to some degree (depending on relative thicknesses of the other layers), while the other layers become strained to some degree, with a strain of the opposite sign of the initial layer. Thus if a SiGe alloy layer is grown on (unstrained) Si, this alloy layer is strained compressively in the plane (biaxially), because the lattice constant of Ge is ~4% larger than that of Si. If a Si layer is grown on top of the alloy layer, it will be unstrained until release (like the original Si layer). When the sandwich is released, both Si layers will become tensilely strained while the SiGe alloy layer will become less compressively strained (all biaxially, in the plane). If the thicknesses of the sandwiching layers are the same, the strain release will be balanced and the membrane will be flat; if not it will curl. Figure 1 illustrates the growth, release, and transfer sequence. Figure 1 (e) shows a three-layer strain-balanced membrane after it settles on the handle wafer after etching through the oxide. It is very rumpled, but nevertheless single-crystal. Figure 1 (f) shows the same membrane after it is floated off the handle wafer and deposited on a host wafer. It is flat, as expected; the perfect crystallinity can be confirmed with x-ray diffraction. Figure 2 shows a particularly striking example of the result of unbalancing the strain – the formation of hundreds of identical tubes. [11] The figure illustrates a very significant fact of nanomembranes: because effectively top-down fabrication methods are used, thousands of identical structures can be made and assembled, in contrast, for example, to VLS wire growth methods, CVD nanotube growth, or the mechanical assembly of individual, selectively sorted nanotubes.

**Figure 1.** Elastic strain sharing Si nanomembrane fabrication process and resulting membranes. (a) Deposition of pseudomorphic (hence strained) layer on thin Si template. Overgrowth with Si if desired. (b) Patterning of access holes for etchant (desirable in most cases). (c) Etching. As the oxide is undercut, the membrane settles on the handle wafer. (d) Membrane transfer to new host. (e) Optical image of a single-crystal nanomembrane that has settled on the handle wafer after etching (step (c)) [courtesy Michelle Roberts]. Optical image of a piece of 0.5 x 0.5 cm membrane transferred to an oxidized Si wafer. The membrane is flat.
Figure 2. Optical image of an array of ~300 Si/SiGe microtubes fabricated by patterning a SiNM sheet before release and then etching. After Ref. 11. A multimedia video of the “birth” of these tubes can be enjoyed at http://www.iop.org/EJ/mmedia/1367-2630/7/1/241/ The lower image shows an individual tube [courtesy Robert Blick]. The overlap of the Si membrane at the “joint” is clearly observable.

Extending this concept, the nanomembrane approach also lends itself extremely well to nanowire or nanoribbon fabrication. The only requirement is a 2D lithography that is capable of nanometer dimensions. There are several choices: nanoimprint lithography, electron beam writing, and UV laser or soft-x-ray interference lithography. Figure 3 shows Si nanoribbons made via e-beam lithography in SOI. Patterns made in two directions, <100> and <110>, are shown, illustrating that it is straightforward to select particular directions based on a specific need for mobility, band structure, surface sensitivity, or thermal conductivity. Wires from multilayer strained nanomembranes can also be made; they will, of course, be bent upward or downward if SiGe is grown on Si and both ends of the wire remain attached. If one end of the wire is cut from its membrane support, the wire will curl or not, depending on whether the strain has been balanced. Fig. 3 (b) shows released curled strips of different lengths.

Figure 3. SEM images of nanoribbons patterned from strained Si nanomembranes and then released. Top panel: ribbons attached at both ends, cut in two different directions <110> and <100>, width ~ 300nm (~500nm for the left figure), thickness ~25nm, length 5-10 micrometers. The left part of this figure is taken at 45 degrees and thus the Y distance is foreshortened. [Courtesy Clark Ritz]. Bottom panel: ribbons released at one end and cut in a direction to form spirals rather than rings. Ribbon width 200nm, length varying from several hundred nm to 10’s of micrometers. [Courtesy Michelle Roberts and Frank Flack].

Returning to tubes, the ones shown in Fig. 2 are approximately 10 micrometers in diameter, not exactly nano-size. How small can they be made? That depends on the materials combination and the relative thicknesses. [12] Figure 4 plots the diameter of a Si/Ge nanotubes using pure Ge deposited on pure Si. [13] For a 2nm Si layer, ~60nm dia tubes would be achievable with approximately 1.7 nm of pure Ge. Thicker Ge will produce smaller diameters, but there is a problem that Ge begins to form 3D islands. They still stress the Si, but to a lesser degree because the 3D island formation relieves some
of the stress. One can also imagine starting with a layer of Si that is thinner than 2nm. Ultimately several atomic layers of pure Ge grown pseudomorphically on one atomic layer of Si and then released theoretically produces a tube diameter that rivals that of single-wall nanotubes. 10nm diameter Si/Ge tubes have already been made some years ago. [15]

As suggested above, using the additional parameter of elastically “soft” directions in a membrane by patterning strain unbalanced membranes along particular directions and into rectangles with various aspect ratios can produce coils, “drills”, or spiral tubes, [15] as shown in Figure 5. In fact, the curling of the ribbons shown in Fig. 3 indicates the effect of direction of cut. Fabrication rules for 3D architectures can be found in Ref. 12.

![Graph](image1)

**Figure 4.** Calculation of Si nanotube diameter (in Angstrom) as a function of the original unstrained-Si thickness, for three different mean thicknesses of pure Ge grown pseudomorphically on the Si and two directions of cut. [Courtesy Feng Liu, after Ref. 13].

![Images](image2)

**Figure 5.** Images of the coiling of a nanomembrane sheet under different cut directions, producing variously a “twisted spaghetti (Fusilli)” coil, a “drill”, and a rolled tube with overlaps. The tube is 5 micrometers in diameter. [Courtesy Robert Blick].

**Localized strain**

All the fabrication rules invoked above imply uniform, global strain over the membrane, produced by a heteroepitaxially grown pseudomorphic film. We know, however, that it is easy to form 3D coherent (lattice matched, pseudomorphic) islands in the Stranski-Krastanov growth mode. [16] We also know that these (hut and dome) islands exert enough local strain to bend the Si template layer on SOI. [17]
The same effect can be studied on free membranes. X-ray microdiffraction allows looking at just one or a few nanostressors and the strain produced by them, via a local-curvature measurement. The results show a tensile strain of the Si of >0.5 % at the Ge hut/Si membrane interface. The lateral extent of the strain in the Si extends over perhaps twice the lateral size of the nanostressors. As briefly described below, strain affects band alignment and band offsets. It should therefore be possible to induce local “quantum wells” caused by strain.

**Surface transfer doping**

The total number of dopants per unit area becomes small when a crystal is made thin, causing the sheet resistance to increase. Additionally, surface or interface states can potentially trap charge carriers, making a thin enough semiconductor sheet (or ribbons and even wires) truly intrinsic in its electronic behavior. For example, there are $10^{10}$ dopant atoms in one cm$^2$ of a 100 nm thick Si membrane doped at $10^{15}$ cm$^{-3}$. There are $\sim 10^{11}$ cm$^{-2}$ interface states at an oxide/Si interface that can trap charge. If only 1/10th traps mobile charge carriers, the 100nm thick Si membrane will be intrinsic. Yet under the proper circumstances, the membrane can conduct as well as bulk Si.

The “proper circumstance” here is the introduction of “surface dopants”. These need not even be new or different atoms, but only a properly positioned density of states associated with the existence of a surface, as shown in Fig. 6. In Si(001) the dimer reconstruction creates $\pi$ (HOMO – highest filled molecular orbital) and $\pi^*$ (LUMO – lowest unoccupied molecular orbital) bands that are positioned relative to the bulk bands of Si such that a much narrower gap exists for thermal excitation of (in this case) electrons than the bulk (intrinsic) gap. The excitation is into the $\pi^*$ band, which is (depending on the source of the information) variously between 0.35 and 0.6 eV away from the top of the bulk valence band. The current is high, and no matter how thin the membrane is, conduction should be possible if the surface bands exist.

The tip-off for existence of this effect came from the ability to image a very thin (10nm) Si template layer on SOI and then recognizing that such a thin layer was bulk depleted and therefore intrinsic. Figure 6 (b) shows an example. In some sense, the images were disappointing, as they look just like corresponding images from bulk, conventionally doped Si, measured at the same STM conditions. Because of the sensitivity to the surface condition, which affects (in Si(001)) the availability of final states for thermal excitation, conductivity in the membrane should be controllable by tailoring the position of HOMO and LUMO bands of organic or inorganic atomic or molecular layers on the surface.

**Membrane heterostructures**

Any multilayer strain-relaxed membrane is a heterostructure with band offsets that differ from an unstrained system, because strain changes the band offsets. So, for example, tensilely strained Si between two layers of relaxed SiGe produces a quantum well in the conduction band, while a compressively strained SiGe layer between two relaxed Si layers produces a quantum well in the valence band. When a grown heterostructure is released from its handle wafer and elastic strain relaxation takes place, the band offsets change. Strain can now become a parameter in the design of vertical-transport heterostructures and in the design of two-dimensional electron gases and voltage

Figure 6. Schematic diagram of the surface transfer doping effect observed in Si nanomembranes and STM image of the surface of a 10nm Si template layer. The positions of the surface bands produced by the dimer rows shown in the STM image relative to the bulk valence band make possible the thermal excitation of electrons from the bulk valence band, and thus high-mobility bulk hole conduction. [Image courtesy Pengpeng Zhang]
controlled quantum dots. It has been possible to compare quantum wells in released and unreleased membranes, with a clear effect in the magnetoresistance, demonstrating that the elastic strain sharing upon release of a membrane changes the band offsets sufficiently to change the bound states inside the well. [7]

Conclusions
Thin semiconductor membranes represent a new nanosystem with very high potential for both technology and novel science. The essentially top-down fabrication approach avoids the issues associated with bottoms-up approaches, while still exhibiting the potential suggested by nanotubes and nanowires. The ability to make many identical structures gives the nanomembrane processes an advantage in terms of incorporation into technology. Independent of this potential, many interesting avenues for scientific exploration of membrane nanoproperties beckon.

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