Semiconductor Nanomembranes: A Platform for New Science and Technology

M. G. Lagally, A.M. Kiefer, D. M. Paskiewicz, F. Cavallo, S. A. Scott, Z.Q. Ma, and D. E. Savage
University of Wisconsin-Madison, Madison WI 53706

ABSTRACT

Semiconductor nanomembranes, extremely thin (<10 to ~1000 nm) single-crystal sheets, promise considerable new science and technology. They are flexible, they are readily transferable to other hosts and conform and bond easily, and they can take on a large range of shapes (tubes, spirals, ribbons, wires) via appropriate strain engineering and patterning. The ready ability to stack membranes allows the integration of the properties of different materials and/or orientations. A brief review of nanomembrane fabrication and manipulation with a view toward different types of applications is provided.

Keywords: Nanomembranes, semiconductor, strain engineering, heteroepitaxy, integration.

1. INTRODUCTION

Semiconductor nanomembranes, which promise to become a disruptive platform for both new science and new technology, owe their existence to a combination of highly refined methods in nanomaterials science. Primary among these is heteroepitaxy, but equally important are selective etching methods and, for some materials, ion implantation and wafer bonding. Epitaxy is a venerable field, discussed in the literature for almost a century. [1, 2] Yet there continue to be new discoveries, which expand upon the original ideas to explore both thermodynamic and kinetic behaviors related to interactions, activation barriers, and the influence of disorder and of strain. Ultimately, of course, epitaxy cannot violate thermodynamic rules, but because growth is innately a non-equilibrium phenomenon, kinetic considerations dominate most outcomes. It is therefore essential to recognize what these limitations are and how one can manipulate them to create materials in thin-film form with novel properties, or, in some cases, entirely new materials.

One area in which the opportunities for new materials or novel properties are especially great is epitaxy involving strained layers. Recent significant progress has come when it was recognized that much more strain can be accommodated by thin sheets than can be accommodated by thick bulk wafers or crystals. [3] A related property is the flexibility of thin sheets relative to bulk materials, which additionally leads to the ability to bond membranes of dissimilar materials, where bulk wafer bonding is impossible or much more difficult.

The role of strain in epitaxy is well known for the conventional growth of a thin film on a bulk substrate. The heteroepitaxy of SiGe alloy on Si provides the model. Ge has a ~4% larger lattice constant than does pure Si; hence a SiGe film grown on bulk Si will be compressively strained. As the film becomes thicker, the strain energy increases until the elastic limit is reached at the critical thickness and the film relaxes via dislocation formation. There is both a thermodynamic and a kinetic critical thickness, the latter being growth temperature dependent (see Fig. 1). [4-6] A strained film can relax by one of two competing mechanisms, via the above described dislocation formation or via the formation of 3D coherent (i.e., lattice matched) nanocrystals (variously called 3D islands, “huts”, nanoclusters, or “quantum dots”). Excessive strain energy tends to be released plastically by dislocations when the strain is relatively small, i.e., for a low-Ge-concentration SiGe alloy on Si(001). For films with larger misfit strain, e.g., pure Ge on Si(001), the system prefers coherent 3D nanocrystal formation after the 2D-film critical thickness is exceeded. The nucleation barrier for formation of 3D nanocrystals decreases rapidly with strain as ε^{-4}, while that for dislocations is linear with ε^{-1}. [7] Coherent 3D nanocrystal formation is an example of the Stranski-Krastanov growth mode. [8] These strained 3D nanocrystals, which have an epitaxial relationship with the substrate, provide an avenue for strain relief that allows more material to grow epitaxially without dislocation formation than the critical thickness for 2D layers allows. The nanocrystals can relieve stress because, even though they are coherent with the substrate, their lattice constant can increase vertically in the struc-

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ture, to be closer to the natural lattice constant of the heteroepitaxial material. The ability to relax vertically to relieve strain allows more heteroepitaxial material to be deposited before extended defects are introduced. The process can become important in creating new materials via the nanomembrane platform.

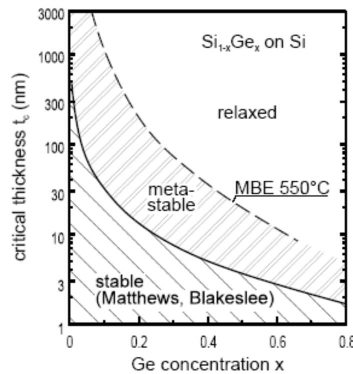

Figure 1. Graph of thermodynamic and kinetic critical thicknesses of a strained SiGe film on Si, as a function of Ge concentration. The kinetic critical thickness is temperature dependent and is shown for a typical growth temperature of 550°C. After Ref. 5.

2. NANOMEMBRANES

The fabrication of thin crystalline films via pseudomorphic growth on a different substrate is over fifty years old. The discussion above describes the conditions under which a thin film remains single-crystal without the formation of extended defects. These thin films are not referred to as nanomembranes. In the most general view, a nanomembrane is a thin sheet of material that is either physically or electrically isolated from the bulk substrate. Physical isolation results if in some part of the fabrication process the sheet is freed from the constraints of the substrate and transferred to a new host. A crystalline nanomembrane can be formed from a pseudomorphically grown stack if one of the layers in the stack can be differentially etched with a high selectivity. Examples are found in the III-V semiconductors, where, for example, Al can be added to GaAs to make GaAlAs, which etches quite differently from GaAs, or InGaAs can be deposited on InP, which etches selectively. A different approach with the same end purpose uses wafer bonding of dissimilar materials with the bonding layer the one that selectively etches. The primary examples occur in Group IV materials, in particular silicon-on-insulator (SOI) and its variants. In such cases, of course, one of the wafers that are bonded must be able to be thinned. With Si this is accomplished typically by ion implantations of H and subsequent annealing, which allows the wafer the crack at the depth of the implant (the Soitec SmartCut^{TM} technique), and subsequently polished and thinned further. If Si is bonded to oxidized Si (standard SOI) the result is a thin "template layer" of Si (of the order of one hundred to several hundred nanometers) separated from a thick Si wafer by SiO_2 of a desired thickness, usually less than several microns to as little as 100s of nm. Other materials can be bonded and thinned in the same way, so that it is feasible to make Ge-on-insulator (GOI) or SiGe-on insulator, among other variants.

The nanomembrane (NM) then results if the oxide is selectively etched to free the thin template layer. Different thicknesses of NMs are possible by thinning the template layer before the selective etch of the oxide. Figure 2 shows a schematic diagram of SOI and a resulting SiNM laid on a TEM grid. The SiNM is ~100nm thick and is a perfect single crystal. One can see that it is transparent.

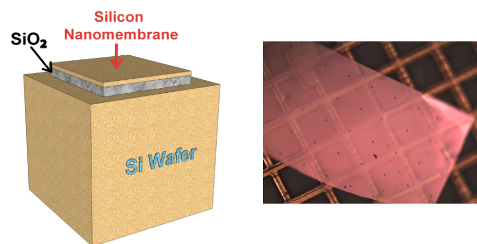

Figure 2. Schematic diagram of SOI and a SiNM selectively etched and transferred to a TEM grid.

3. HETEROEPITAXY AND STRAIN SHARING IN NANOMEMBRANES

Despite the physical insight into the development of lattice strain in heteroepitaxy and the influence of strain in ordering and in creating defects provided by past work, all of the effort has focused on epitaxy on substrates that are much thicker than the growing film. It is only quite recently that systems have been considered in which the substrate is not thick. The way the strain is shared between a growing film and the substrate begins to change as the substrate gets thinner. The growing strained film applies effectively an "external" stress to bend and stretch the substrate. Conventionally, when the deposited film is much thinner than the substrate, bending dominates (even though it is ignored because it is so small) and increases linearly with increasing film thickness, following the classical Stoney formula. [9] The behavior deviates dramatically from the classical linear dependence when the film thickness becomes comparable to the substrate thickness, or, more correctly, when the substrate becomes thin enough so that it approaches the heteroepitaxial-film thickness.

The behavior can be understood by considering the evolution of strain sharing between the film and thin substrate. Strain sharing affects critical thicknesses and defect formation in heteroepitaxy and produces most interesting results in nanoepitaxy. Suppose we grow a tensilely strained pseudomorphic film on a thin substrate. The tensile strain in the film is relaxed (reduced) at the expense of introducing a compressive strain in the substrate, i.e., by sharing strain with the substrate, through both bending and uniform expansion. In general then in a bilayer (film + substrate) system, lattice misfit stress imposed via heteropitaxy leads to bending. The recognition of this phenomenon opened a new field of study, starting in approximately 2000. [10,11] If a thin crystalline film is grown on another thin crystalline substrate to produce large lattice strain, the combination will curl. As mentioned in Sec. 2, this technology became feasible through the use of release layers, i.e., layers that have large differential etch rates relative to the desired film couple. Figure 3 shows the process schematically, along with an image of a resulting Si/SiGe microtube. [12] There are many reliable release layers for many different materials; for Si the most common is SiO_2.

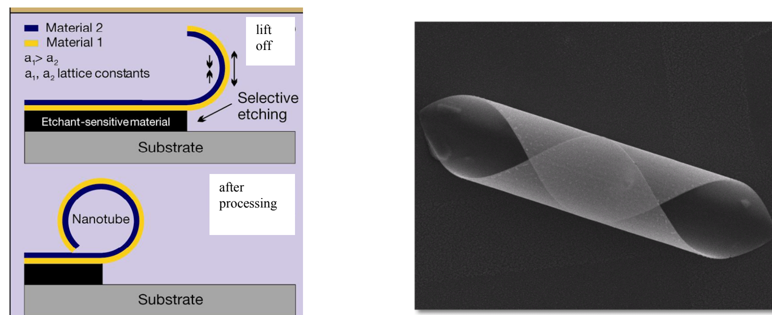

Figure 3. Strain sharing in bilayer sheets to create 3D nanoarchitectures. Left: Schematic diagram of release, via selective etching, of a bilayer with large differential strain, causing rolling. Courtesy of Oliver Schmidt. Right: Scanning electron micrograph of a ~10 micron SiGe microtube, fabricated by depositing an epitaxial layer of Si onto crystalline SiGe and releasing the combination from the underlying silicon dioxide. From Ref. 12. Image courtesy of Robert Blick.

Although the above example involved heteroepitaxy, crystalline layers are not necessary to produce curling or bending; any combination of materials producing differential stress will curl or roll (for example, bimetallic strips used in thermostats use differential thermal stress to bend). With proper patterning of shapes and taking advantage of anisotropies in elastic constants of the film materials one can create an amazing number of different "nanoarchitectures". [12]

Nanoarchitectures, such as those shown in Fig. 3, exhibit many unique physical phenomena and have many potential applications (including most recently in the semiconductor/biology interface [13]), but in many situations are limiting. Most progress relevant to semiconductor electronics and optoelectronics has instead been made using strain sharing trilayers. [3] The epitaxy is the same, but one grows two layers epitaxially on the thin functional substrate, rather than one, resulting in a trilayer instead of a bilayer. The middle layer of this sandwich is strained, and the top layer is grown to a thickness appropriate to balance the bottom layer. When the trilayer structure is released, the strain initially induced in the central layer is shared equally with the two outer layers and the structure remains flat. For Si nanomembranes (SiNMs), the fabrication approach involves, for example, epitaxial growth of a strained-SiGe thin film (the stressor layer) on an ultra-thin Si template layer of silicon-on-insulator (SOI), followed by an epitaxial Si layer over the SiGe

film, and subsequent etching of the buried oxide layer. The outer Si layers of the trilayer may be as thin as 10nm or up to 100nm, depending on the strain transfer desired. The trilayer relaxes via elastic strain sharing between the layers, generating defect-free tensilely strained Si layers. The trilayer can be transferred and bonded to almost any other surface, [3] offering many opportunities to integrate defect-free strained films where direct growth is not possible, such as in high-speed flexible electronics or novel optoelectronics. Recent reviews have described the extent of applications and physical phenomena whose exploration is enabled by nanomembrane epitaxy. [14,15]

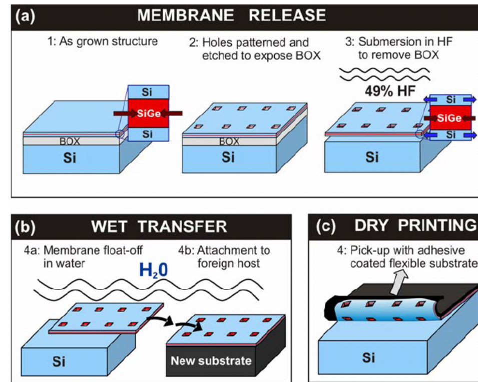

Figure 4. Schematic illustrations of the membrane release and transfer processes: (a) 1: An as-grown heterostructure membrane consisting of a Si/SiGe/Si layer where the first Si layer is composed of the template layer of SOI; the SiGe layer is compressively strained. 2: The as-grown structure is patterned with an array of holes that provide etchant access to the BOX. 3: The BOX layer is removed with hydrofluoric acid (HF), releasing the membrane, and allowing relaxation via elastic strain sharing. Compared to the pre-release membrane, the final released membrane has a less compressively strained SiGe layer sandwiched between two tensilely strained Si layers. (b) The wet transfer process involves floating the membrane from its resting place on the handling substrate, and transfer in solution to a new host surface. (c) The dry printing technique involves transferring the membrane to a flexible host by coating the host with adhesive material and bringing it into contact with the resting membrane. From Ref. 14.

These trilayer sandwiches involve only elastic stress-strain relationships, so that no dislocations form. In other words, the critical thicknesses for dislocation formation discussed in Sec. 1 have to be respected, but allowing for 3D nanocrystal formation to get greater thicknesses of the middle stressor layer or higher strains, as required. A number of materials with new properties or new strain configurations can result.

1. A strain relaxed trilayer nanomembrane, consisting in the particular case we are discussing here of tensilely strained Si, compressively strained SiGe, and tensilely strained Si, can be transferred and bonded to a new host. The top two layers of the sandwich can be removed, leaving a dislocation-free tensilely strained Si layer. The band structure of this strained Si will differ from unstrained Si, with different orientations of the Si (e.g., (001) or (110)) producing different band splitting and band shifting. [16,17] Such band modifications, especially in the conduction band, have significant implications for quantum electronics [3] and for mobility enhancement in thin-film transistors. [18]
2. The same strain relaxed trilayer nanomembrane can be processed while in the free state so that both of the tensile-Si layers are removed, leaving then a completely elastically relaxed single-crystal membrane of SiGe, i.e., without dislocations. Defect-free uniform single-crystal SiGe cannot be made any other way. Using epitaxy to the extent of forming the 3D nanocrystals described above allows high-Ge-concentration alloys to be made. [19] These SiGe membranes, when transferred and bonded to a new host, can be used as substrates for growing a defect-free thick SiGe crystal, or as substrate for growing strained-Si two-dimensional electron gases (2DEGs).
3. By combining layers with different symmetries in the trilayer sandwich, one can change the strain symmetry in a nanomembrane in a way that is not the bulk symmetry and is not possible to do any other way. [20] So, for example, we can produce biaxial strain in materials that have a lower elastic symmetry and would by other growth techniques produce only uniaxial strain. Because electron transport and band structure depend on strain symmetry, we may be able to produce novel electronic properties in semiconductors or eventually oxides.

4. EPITAXY ON NANOMEMBRANES

In the last sections we described how one can, via the combination of heteroepitaxy and release of thin sheets of crystalline material, create novel strain conditions and strained structures, both with 3D shapes and with 2D shapes. In addition to the two generic cases considered (1. epitaxy of bilayers combined with patterning to produce 3D objects and 2. epitaxy in tri- or multilayer structures to create novel strain conditions that cannot be achieved on bulk, because they require the release step to develop), there is another situation: epitaxy directly on free-standing membranes. The latter creates novel behaviors, because now the membrane participates in the strain sharing from the initial stages of growth, and can relieve strain in the growing film much more effectively. Because the substrate is a thin membrane, it will accommodate more of the strain than a thick substrate would. For epitaxy of a 2D layer, the critical thickness will be larger, and some bending should occur.

If nanostressors are grown on a nanomembrane, i.e., not a 2D film but a 3D nanocrystal, the stress is local and can be periodic. A nanostressor can locally bend the thin substrate. [21-23] The thinner the substrate membrane, the more it bends and the more strain it accepts relative to the nanostressor. For a free-standing NM, with chemical vapor deposition as the deposition mode, growth of hut nanostressors on both sides of a thin-free-standing membrane is enabled. They self-organize into a periodic pattern, producing periodic strain in the Si membrane. [24, 25] The periodic strain in the Si membrane produces a periodic modulation of the band gap, and thus a 1D strain-generated electronic heterojunction superlattice. Generally electronic heterojunctions involve at least two chemically distinct materials; here we have produced a single-element heterojunction, in which strain provides the band offsets. [25] Depending on the magnitude of the strain, the period of the strain, and the thickness of the NM, one can obtain Type I, Type II, or mixed electronic superlattices. [26] The approach of forming single-element periodic strain lattices – and thus electronic superlattices - should be general and can be expanded to lithographically patterned nanostressors to provide the period strain field.

5. BRIEF EXAMPLES OF POTENTIAL APPLICATIONS

Nanomembranes have been at the center of research on a number of directions to create usable technology. Probably the most advanced is fast flexible electronics and optoelectronics. Figure 5 shows an image of flexible thin-film transistor (TFT) circuits along with data showing the very high speed that is achievable. [27] There are many possible applications, especially as passives can also be fabricated on the flexible substrate, so that complete circuits are possible.

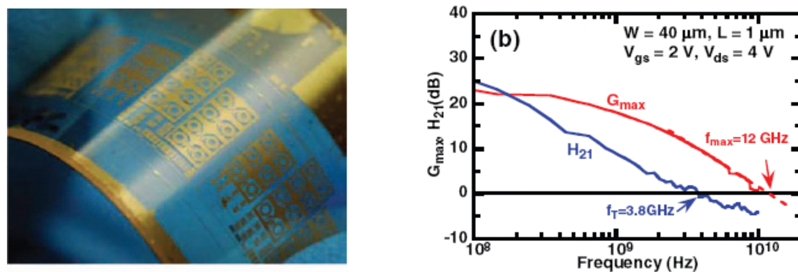

Figure 5. Image of a TFT array on a bent PET substrate and TFT characteristics. a) optical image, b) measured frequency response characteristics of the TFT under V_{gs} = 2 V and V_{ds} = 4 V. From Ref. 27.

A result in the same class is a flexible lateral photodetector, implementing a Ge lateral P-I-N diode. A 100nm Ge NM is transferred to a flexible host (PET), and implanted with n and p-type regions, with a narrow intrinsic region between them. The efficiency of the device is quite high. [28]

In the above, charge transport is in the lateral direction. Also of considerable interest is transport in the vertical direction, across interfaces of stacked membranes. Such structures will be essential for photodetectors, photovoltaic cells, and potentially light sources. Stacked nanomembranes allow configurations of materials not achievable with conventional epitaxy on rigid supports. Figure 6 shows an example of a vertical tunneling junction made by transferring a thin Si membrane to a patterned Ge host and bonding it there. [29] The interfaces are extremely good, and a high current can pass across the interface. Such results provide optimism that much more complex structures can be fabricated by combining nanomembranes of different materials. For example, the ability to stack and bond makes semiconductor NMs versatile building blocks of hybrid metal/semiconductor or dielectric/semiconductor structures. Stacks of silicon mem-

branes separated by metal/dielectric layers are important, as the silicon layers can preserve their crystalline structures when layers are stacked instead of grown. Such hybrid structures are of interest in nano-optics, where light can be coupled to surface plasmons in metal layers for on-chip based optical characterization of molecules or nanostructures. As has been shown, the same concept of stacked hybrid layers can be used for creating Bragg mirrors (1D diffraction gratings). [30]

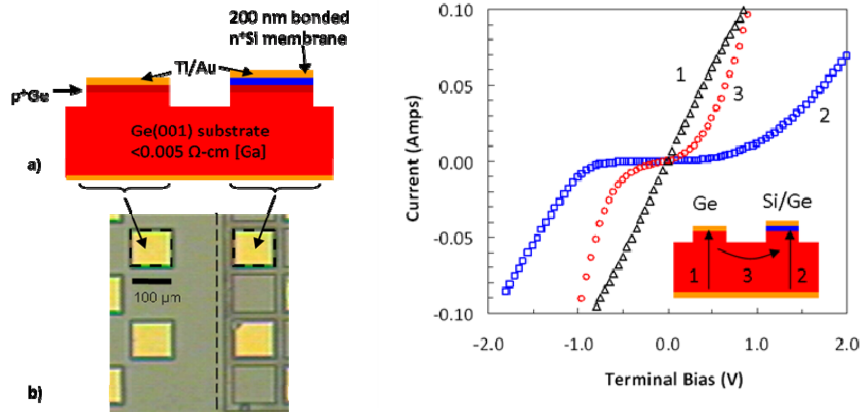

Figure 6. Device structure for cross-interface charge transport measurements and results of such measurements. Left: (a) A schematic diagram of a cross section of a mesa-type Si/Ge diode and (b) an optical micrograph of Ge mesas (left) and Si/Ge mesas (right) used for charge transport measurements. Right: I-V measurement; path 1 (Δ) Ge mesa to Ge back contact showing ohmic behavior; path 2 (□) Ge back contact to Si/Ge mesa; and path 3 (○) Ge mesa to Si/Ge mesa. From Ref. 29.

Nanomembranes also offer a natural confinement in one dimension combined with the possibility to cover large areas. Using standard microcontact printing or laser interference lithography, large-area arrays of nanowires or nanoribbons with diameter (widths) down to 20 nm can be patterned. The diameter of the wires can be further reduced by selective wet chemical etching of the silicon. [31] The periodic pattern and large-area coverage is a prerequisite to integrate nanowires in most device processing that requires semiconductors, including photovoltaic and thermoelectric energy conversion devices, sensors, and detectors of various sorts. With the flexibility in transferring the membrane to almost any substrate, this approach is attractive for developing devices on technologically relevant substrates like flexible polymer, quartz, SiC, or GaAs. Advantages of nanowires fabricated from membranes compared with vapor-liquid-solid (VLS) grown nanowires are the uniformity of the nanowire diameter, large-area coverage of periodically positioned nanowires, and the possibility to control the crystalline directions along the nanowire. Pure silicon or doped wires can be fabricated through this process, avoiding the difficulty associated with metal incorporation and dopant control in VLS methods.

6. SUMMARY

This brief review has aimed to demonstrate how epitaxy, strain, and super-thin substrates can combine to lead to totally new physical phenomena. Adding strain in growth, along with release processes that allow that strain to be shared, creates many opportunities. Thinness of the substrate and strain engineering through multilayer membrane epitaxy and membrane stacking produces new insights, new materials with properties not attainable in other ways, and new approaches for fabricating novel device structures in electronics, optoelectronics, and potentially photonics.

7. ACKNOWLEDGMENTS

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