Group IV nanomembranes and nanoepitaxy: New properties via local and global strain engineering

Francesca Cavallo, Deborah M. Paskiewicz, Shelley A. Scott, MingHuang Huang, and Max G. Lagally
University of Wisconsin-Madison, Madison, Wisconsin 53706, USA

ABSTRACT

Semiconductor nanomembranes, single-crystal sheets as thin as ten nanometers, offer many opportunities for novel devices and new science. The most interesting involve epitaxy to introduce strain at both local and global levels. Coming into play are membrane thinness, access to both sides of a sheet, transferability, and enhanced compliancy. Advances in Group IV optoelectronics, thermoelectrics, and photonics may be achievable by combining epitaxy with Si and Ge nanomembranes. Nanoepitaxy allows formation of new strained materials, periodic strain lattices, and mix and match membranes with hybrid orientations or compositions.

Keywords: semiconductor, nanomembranes, epitaxy, silicon, strain, quantum dots

1. INTRODUCTION

A recently developed approach in semiconductor technology, based on the use of crystalline nanomembranes as an alternative to bulk substrates, promises to expand the range of application of particularly Group IV materials.[1-11] Nanomembranes (NMs) are distinguished from bulk materials most significantly by thinness, flexibility, and the nearness of two surfaces or interfaces, as well as by easy bondability, conformability to other shapes, and stackability. Excellent and in many cases unique structural, electronic, and optical properties have been measured, both for flat and for curled or rolled nanomembranes.[1-17] Furthermore, the ability to transfer released NMs to a large variety of hosts has been successfully used for the fabrication of hybrid or highly lattice mismatched single-crystal multilayer stacks, and for the development of bendable and stretchable electronics.[2,16,17] Nanomembrane-based device structures typically combine top-down and bottom-up approaches to achieve a high degree of control on self assembly;[12-14] they can be completely free-standing or tethered to a substrate, and they can be flat[3,12] or shaped in three-dimensional (3D) structures.[13,14] Most effort has been dedicated to Group IV materials because Si forms the core of our computing and communication, as well as energy conversion, technologies.

Although there are already many demonstrations of applications of Si nanomembranes (SiNMs) that are based on their flexibility and the ability to process these SiNMs in the same manner as bulk Si, the most promising and exciting efforts combine epitaxy with nanomembranes via their thinness and mechanical compliance. One can, for example, use epitaxy to establish a uniform or spatially varying strain field in the ultra-thin crystalline sheet.[3,12,18-21] Epitaxy can create elastic strain sharing between a SiGe and a Si film completely unsupported by a solid to create perfectly dislocation-free tensilely strained SiNMs.[3,12,19] Similarly, a spatially varying strain field can be established in Si nanoribbons by growing "local stressors" (e.g., Ge quantum dots (QDs)) rather than a "uniform stressor" (e.g., a SiGe strained layer).[18,20] Strain engineering of SiNMs offers the possibility of tuning materials properties, such as band gap and carrier mobility, both on a global and a local scale. This capability has significant implications for development of a membrane-based technology for the fabrication of high-performance and novel electron device structures,[2,3,17] as well as nanoscale photonic and thermoelectric devices.[22]

We focus here on recent developments for which epitaxy plays the critical role in creating a new material or new properties. These include the use of epitaxy and elastic strain-sharing to fabricate biaxially strained (110)-oriented SiNMs, not possible any other way; the use of epitaxy and membrane layering and bonding to create crystalline, hybrid-orientation or hybrid-composition NM "quilts"; and the use of double-sided QD epitaxy on free-standing NMs, taking advantage of

through-membrane elastic interactions, to cause the ordering of nanostressors that locally and periodically highly strain the NM to create a strain superlattice.

2. EPITAXY AND STRAIN

The role of strain in epitaxy is well known for the conventional growth of a thin film on a bulk substrate. In SiGe/Si the ~4% larger lattice constant of Ge implies that 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).[23, 24] A strained film can relax by one of two competing mechanisms, via dislocation formation or via the formation of 3D coherent nanostressor islands.[25] The strain energy tends to be released plastically by dislocations when the strain is relatively small, i.e., for a thick enough low-Ge-concentration SiGe alloy on Si(001). For
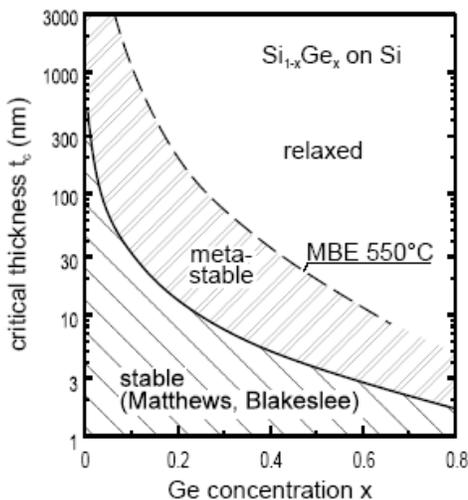

Figure 1. Graph of thermodynamic and kinetic critical thicknesses of a strained SiGe film on Si, as a function of Ge concentration. The kinetic critical thickness is shown for a typical growth temperature of 550C. After Refs. 23 and 24.

films with larger misfit strain, e.g., Ge on Si(001), the system prefers 3D island formation after the 2D-film critical thickness is exceeded.[26] These strained 3D nanoclusters, which have an epitaxial relationship with the substrate (until they become too large and dislocate at the interface), provide an avenue for strain relief that allows more material to grow epitaxially without dislocation formation than the critical thickness for 2D layers allows.[25]

These 3D nanostressors, which have been studied in great detail,[27-29] form on top of a wetting layer whose thickness is controlled by the composition and the degree of strain that can be accommodated by the Si substrate, either via curvature or via expansion of the substrate (as discussed below).[29, 30] Figure 2 shows Ge nanostressor "islands" growing in ordered patterns in regions where the curvature is the highest, but where the space for growth is not confined *per se*. The nucleation there is a function of the strain term that is inherent in the wetting layer and of the curvature.[30] Strain is noticeable already in the first Ge layer that is deposited.[31] Via the deposition of Ge on vicinal Si(001) and the resulting influence of strain on the step structure, the contribution of the Ge-deposition-induced strain free energy to the surface energies can be quantified.[32] The defined addition of Ge furthermore allows extraction of the dimer-reconstruction-induced surface stress anisotropy for clean Si(001).[33]

The nanoepitaxy inherent in "quantum dot" nanostressor formation will be the basis of one of the examples discussed below. The structures are self-organized and local on lateral length scales. Growth on nanomembranes changes the behavior of the self-organization, because the elastic properties of a membrane are different from the bulk and thus a mem-

brane responds differently to the stress induced by the quantum dot. On a different level, we grow through holes in one membrane stacked on another to form a flexible hybrid-orientation (HOT) nanomaterial. In the simplest case strain is
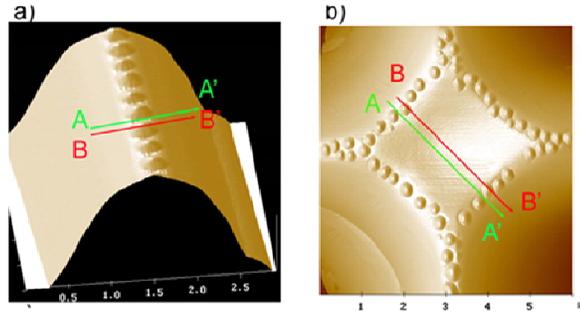

Figure 2: Atomic-microscopy images of 3D nanostressor epitaxy and ordering on regions of high curvature, but structurally otherwise not confined. Red and green lines indicate qualitative periodicity of nanostressors. a) single ridge, b) cross of two ridges. From Ref. 30. Images courtesy of Bin Yang.

not involved (except at the boundaries – the edges of the holes in the upper membrane), but can be, in more complex HOT systems or hybrid-composition systems. The growth is reminiscent of lateral epitaxial overgrowth, except no overgrowth is desired, but rather a smooth flat outer surface. Finally, the most general case involves strain engineering of membranes and release from the host material to create in some cases new materials not obtainable in other ways.

3. STRAIN SUPERLATTICE IN A SI NANOMEMBRANE

As alluded to above, Ge or Ge-rich SiGe QDs act as local nanostressors. When grown on nanomembranes, strain sharing between the QDs and the very flexible SiNM is quite different from that on bulk substrates, creating very small regions of high local strain in the membrane. As a result the NM undergoes local distortion. That the response is different from bulk can be most readily seen in terms of Fig. 3. Although strain is always shared to some degree, a massive bulk accepts much less strain, and thus most strain remains in the thin film. A thin substrate can more readily accept strain and distort (stretch or bend) as the strain is shared.
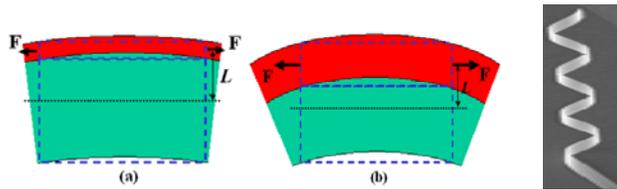

Figure 3. Schematic illustration of the effect of a compressively stressed thin film on a) a bulk substrate and b) a much thinner substrate. The latter can share strain much more effectively. The image at right shows an example of a differential-strain driven 3D nanoshape that can be created by judicious choice of layers, the 2D pattern that is cut (here a strip), and the direction of this cut.

An individual QD can thus create a large local strain in a thin membrane.[34,35] Because the substrate accepts a much larger degree of strain, these QDs can grow larger before dislocating. Similarly, a stressor film covering the whole surface of a free-standing nanomembrane can grow thicker before reaching its critical thickness if the membrane can accept the strain. That is in contrast to the same film growing on a constrained substrate, even if thin, as on the template layer of SOI. There is evidence that the critical thickness is reduced in such cases, because of the ease of dislocation generation and core spreading at the oxide/Si interface.[36, 37]

The large local strain in a thin membrane provides a feedback for self-organization of the QDs that is absent on bulk Si. This feedback is effective if growth occurs on both sides of the NM, something that can be done via CVD but not with MBE. We grow nanostressors on freestanding ribbons or membranes (in the form of a wide cantilever attached at one side to the BOX, but undercut so access is provided to the lower side.[20] Ge or a Ge-rich SiGe alloy is deposited simulta-

neously on both sides of these free-standing nanoribbons using CVD. Because CVD involves the vapor phase transport of precursor molecules, deposition is possible at all locations accessible to the growth gases. The feedback mechanism briefly described above and reported in more details in Ref. [20] leads to a spatially periodic arrangement of pyramid shaped QDs, alternating on the top and on the bottom surface of the SiNMs. Consequently a periodically varying strain is established along a thin single-crystal Si ribbon. Figure 4 shows scanning electron micrographs of these QDs and their local arrangement. Notable is the lack of arrangement and order of the QDs that are growing on the attached (i.e., not free-standing) part of the sample. The template layer is the same everywhere, but on the free-standing part the QDs can grow on both sides. Figure 4(b) shows the QDs on both sides, possible because the NM is so thin that the electron beam can image QDs on both sides. The anisotropic properties of Si in <110> and <001> directions account for this displacement and the orientation of the square arrangement.[38]
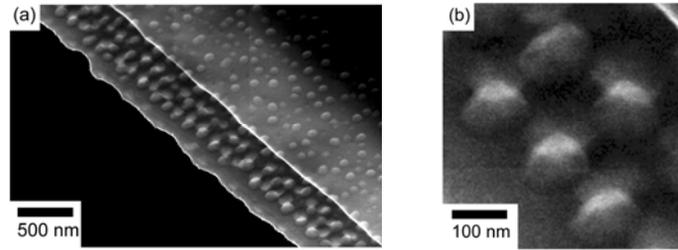

Figure 4. Scanning electron micrographs of QD arrangement on a free-standing membrane if QDs grow on both sides. a) Note the difference in order on the free-standing edge. b) Magnified view shows faint indication of QDs on the underside (vertical displacement). The anisotropic properties of Si in <110> and <001> account for this displacement and the orientation of the square arrangement.

The strain lattice in the Si membrane in turn produces a modulation in the electronic band structure that extends through the thickness of the membrane, and creates an electronic superlattice without a need for compositional modulation, the conventional method for forming electronic heterostructures. In this single-element electronic superlattice, the magnitude of strain tunes the band offset and consequently the type of heterojunction superlattice.[39]

4. HYBRID-ORIENTATION NANOMEMBRANES

Semiconductor nanomembranes have distinct advantages in that they are readily transferable and bondable to other hosts, including other NMs, making possible the transfer of patterns, as one membrane with a pattern can be transferred to another. In addition, one can create new structures by growing strained trilayers. Figure 5 shows the most general case of epitaxy and transfer. The transfer in all cases is initiated with release from the holding substrate, via a highly dif-
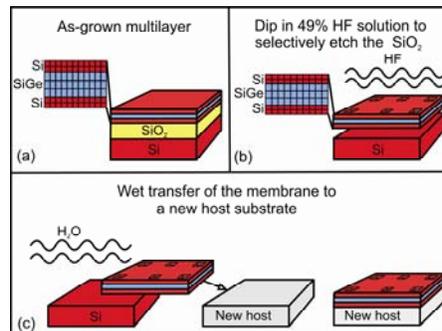

Figure 5. Schematic illustration of the SiNM release and transfer process. (a) As-grown Si/SiGe/Si trilayer. The distribution of the lattice constant across the trilayer is shown on the left hand-side; here the SiGe layer is compressively strained and the Si layers are unstrained. (b) The BOX layer is selectively removed with HF, releasing the membrane and allowing elastic relaxation via lateral expansion. The released trilayer membrane has a less compressively strained-SiGe layer sandwiched between two tensilely strained Si layers. An array of holes is patterned on the unreleased membrane to enhance access of the etchant to the BOX. (c) Wet-transfer process of a released membrane from the original handling substrate to a new host surface. The released membrane can be a single layer or more complex structures that the one shown.

ferentially etchable layer. For Si that layer is SiO_2, as SiO_2 etches hundreds of times faster in HF than does Si. Thus a thin Si layer (or a trilayer membrane as shown in Fig. 5, or some other layer combination) can easily be removed from the holding substrate. Here we consider the fabrication of a hybrid-orientation quilt in membrane form. The transfer of (110) SiNMs to a (001) oriented Si template and subsequent overgrowth can be used to fabricate mixed-crystal-orientation single-crystal semiconductor membranes.[40] The (110) Si template layer is patterned with an array of holes using standard photolithography and RIE, and removed from its handle substrate via selective etching of the BOX layer in HF solution. This procedure creates a temporarily freestanding (110) Si NM, which is then bonded at 500°C to a (001) Si substrate. Typical results are shown in Fig. 6.
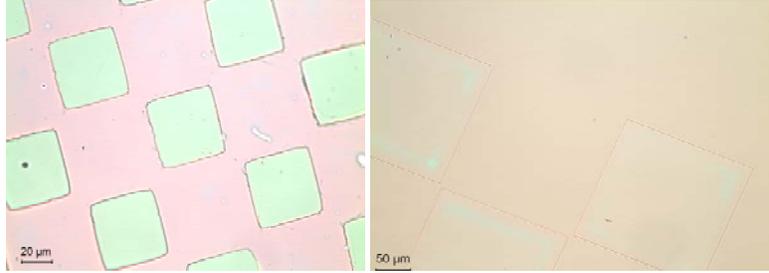

Figure 6. Optical images of hybrid-orientation Si membranes. Left: a (110) oriented membrane (pink) with holes transferred and bonded to a (001) membrane, which can be seen through the holes as green. Right: after growth of (001) Si through the holes until the membrane is planar. The difference can now barely be seen. Si grown via CVD grows 10x as fast on (001) than it does (110), allowing the planarization.

The holes define the regions where the (001) Si crystal planes are exposed through the membrane. Deposition of Si over the structure using CVD with SiH_4 precursor gas, at a substrate temperature of 580°C, fills the holes because the Si growth rate is about 10 times faster on the (001) orientation than on the (110) orientation at 580°C. Hence fabrication of a flat quilt of (001) and (110) Si regions is achieved. Figure 6(b) is an optical-microscope image of a 70 nm (110) SiNM bonded to (001) Si and subsequently overgrown using the growth rate ratio for the two orientations that was determined as described above. The growth front is fairly planar, as indicated by the weak color contrast between the (001) Si and (110) Si areas. The boundary region would typically be removed during shallow trench isolation in device fabrication, so it is of no concern for applications in microelectronics. It would, however, be of interest in any application, such as thermoelectrics, in which charge carrier transport across this region is involved. Such measurements are in progress.

This architecture[40] may allow the manufacture of high-speed flexible electronics, consisting of p- and n-channel devices on (110) Si (high hole mobility) and (001) Si (high electron mobility) regions, respectively, in close proximity to each other, with the benefit of reducing the current drive imbalance between PMOS and NMOS devices.[41] The ability to transfer the HOT membrane structures, after device fabrication, to new hosts opens the possibility for integrating high-speed flexible electronics into a variety of adverse environments and with a variety of shapes.

5. NEW MATERIALS VIA STRAIN ENGINEERING OF NANOMEMBRANES

Figure 5 suggests many ways that new materials can be made via introduction of strain. Some are relatively straightforward. For example, one can make dislocation-free, uniformly tensilely strained Si by growing a Si/SiGe/Si sandwich with all layers below their kinetic critical thicknesses (Fig. 1). High strain and strain uniformity have been demonstrated,[42] as has the increase in mobility using strained Si(001) membranes.[17] One can also make dislocation-free SiGe substrates. Somewhat more esoteric is the ability to make biaxially strained dislocation-free Si(110), and, by extension, create a strain symmetry that does not follow the crystal symmetry. Making biaxially strained Si(110) is, to our knowledge, not possible any other way. We use elastic strain sharing[3,12] in (110) oriented Si/SiGe/Si trilayers to fabricate these strained (110) oriented SiNMs.[19,21]

6. CONCLUSIONS

Semiconductor nanomembranes represent a new paradigm for novel devices and improved performance, particularly for Group IV materials. Epitaxy plays a large role in expanding the promise of these semiconductor nanomembranes. The combination of thinness and flexibility with growth allows strain engineering at both the global and the very local scale. Examples of unique properties and physical effects engendered by combining epitaxy with nanomembranes include nanostressor induced strain lattices that in turn have an electronic heterojunction signature; hybrid-orientation and composition bonded membranes, and new materials in membrane form with unique strain distributions or an absence of extended defects.

7. ACKNOWLEDGMENTS

REFERENCES

[1] Menard, E., Nuzzo, R. G., and Rogers, J. A., Appl. Phys. Lett. **86**, 093507 (2005).
[2] Khang, D. Y., Jiang, H. Q., Huang, Y., and Rogers, J. A., Science **311**, 208 (2006).
[3] Roberts, M. M., Klein, L. J., Savage, D. E., Slinker, K. A., Friesen, M., Celler, G. K., Eriksson, M. A., and Lagally, M. G., Nat. Mater. **5**, 388 (2006).
[4] Yuan, H. -C. and Ma, Z. Q., Appl. Phys. Lett. **89**, 212105 (2006).
[5] Thurmer, D. J., Deneke, C., Mei, Y., and Schmidt, O. G., Appl. Phys. Lett. **89**, 223507 (2006).
[6] Songmuang, R., Rastelli, A., Mendach, S., and Schmidt, O. G., Appl. Phys. Lett. **90**, 919051 (2007).
[7] Mei, Y., Thurmer, D. J., Cavallo, F., Kiravittaya, S., and Schmidt, O. G., Adv. Mater. **19**, 2124 (2007).
[8] Choi, C.–J., Yu, J. B., Geddes, J., Xiao, S., Wang, Y., Huang, Y., and Rogers, J. A., Nature **454**, 748 (2008).
[9] Cavallo, F., Songmuang, R., and Schmidt, O. G., Appl. Phys. Lett. **93**, 143113 (2008).
[10] Yang, H., Pang, H., Qiang, Z., Ma, Z., Zhou, W., Electron. Lett. **44**, 858 (2008).
[11] Yuan, H. C., Shin, J. Y., Qin, G. X., et al., Appl. Phys. Lett **94**, 013102 (2009).
[12] Scott, S. A. and Lagally, M. G., J. Phys D: Appl. Phys. **40**, R75 (2007).
[13] Schmidt, O. G. and Eberl, K., Nature **410**, 168 (2001).
[14] Huang, M., Boone, C., Roberts, M. M., et al., Adv. Mater. **17**, 2860 (2005).
[15] Zhang, P., Tevaarwerk, E., Park, B. -N., et al., Nature **439**, 703 (2006).
[16] Ahn, J. -H., Kim, H.-S., Lee, K. J., et al., Science **314**, 1754 (2006).
[17] Yuan, H. C., Ma, Z. Q., Roberts, M. M., et al., J. Appl. Phys. **100**, 013708 (2006).
[18] Sutter, P., Sutter, E., Rugheimer, P., and Lagally, M. G., Surf. Sci. **789**, 532 (2003).
[19] Optowsky, A. C., Scott, S. A., Ritz, C. S. et al., New J. Phys. **9**, 270 (2007).
[20] Huang, M., Ritz, C. S., Novakovic, B., et al., ACS Nano **3**,721 (2009).
[21] Paskiewicz, D. M., Scott, S. A., Savage, D. E., et al., submitted to Adv. Mater.
[22] Lin, Y. M. and Dresselhaus, M. S., Phys. Rev. B **68**, 0753041 (2003).
[23] Matthews, J. W. and Blakeslee, A. E., J. Cryst. Growth **29,** 273 (1975); **32**, 265 (1976).
[24] Houghton, D., J. Appl. Phys. **70**, 2136 (1999).
[25] Mo, Y.-W., Savage, D.E., Swartzentruber, B.S., and Lagally, M. G., Phys. Rev. Lett. **65**, 1020 (1990).
[26] Tersoff J. and LeGoues, F.K., Phys. Rev. Lett. **72**, 3570 (1994).
[27] Fujikawa, Y., Akiyama, K., Nagao, T. ,et al., Phys. Rev. Lett. **88**, 176101 (2002).
[28] Tomitori, M., Watanabe, K., Kobayashi, M., and Nishikawa, O., Appl. Surf. Sci. **76/77**, 322 (1994).
[29] Tersoff, J., Teichert, C., and Lagally, M. G., Phys. Rev. Lett. **76**, 1675 (1996).
[30] Yang, B., Liu, F., and Lagally, M. G., Phys. Rev. Lett. **92**, 025502-1 (2004).
[31] Chen, X., Zhang, Z.Y., and Lagally, M. G., Phys. Rev. Lett. **73**, 850 (1994).

[32] Wu, F., Chen, X., Zhang, Z.Y., and Lagally, M. G., Phys. Rev. Lett. **74**, 574 (1995).

[33] Wu, F. and Lagally, M. G., Phys. Rev. Lett. **75**, 2534 (1995).

[34] Liu, F., Rugheimer, P.P., Savage, D.E., and Lagally, M. G., Nature **416**, 498 (2002).

[35] Liu, F., M. Huang, Rugheimer, P.P., Savage, D.E., and Lagally, M. G., Phys. Rev. Lett. **89**, 136101 (2002).

[36] Kästner, G. and Gösele, U., J. Appl. Phys. **88**, 4048 (2000).

[37] Rehder, E. M., Inoki, C. K., Kuan, T. S., and Kuech, T. F., J. Appl. Phys. **94**, 7892 (2003).

[38] Kim-Lee, H.-J., Savage, D. E., Ritz, C. S., et al., Phys. Rev. Lett. **102** 226103 (2009).

[39] Liu, Z., Wu, J., Duan, W.H., Lagally, M. G., and Liu, F., Phys. Rev. Lett. **105**, 016802 (2010).

[40] Scott, S.A., Paskiewicz, D. M., Savage, D. E., and Lagally, M. G., ECS Transactions **16**, 215 (2008).

[41] Yang, M., Chan, V. W. C., Chan, K. K., et al., IEEE Transactions on Electron Devices **53**, 965 (2006).

[42] Euaruksakul, C., Li, Z.W., Zheng, F., et al., Phys. Rev. Lett. **101**, 147403 (2008).