Nano-Origami: Art and Function

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To create nanodevices with multiple novel functions, scientists are increasingly inspired and guided by the ancient Japanese art of origami. Just as a piece of paper, extremely thin sheets or strips of crystalline inorganic materials can be rolled, bent, or twisted into new structures but can return to their original shape with application of force. Alternatively, structures can be cut out akin to the variant of origami known as kirigami, producing remarkably artistic 3D nano-objects that respond to a particular stimulus and thus may address a specific technology goal.

Very thin single crystals are not all that new [1]: in the 1970s methods were developed to obtain III-V compound sheets via the selective etching of a sacrificial layer, and science teachers the world over have known for many decades how to use adhesive tape to “peel” single layers of mica or of graphite; the latter we now know as graphene. But it was the description of a commercially viable process for fabricating silicon-on-insulator (SOI) [2], followed by the discovery of many novel electronic properties in graphene that accelerated inorganic-materials sheet science. Crystalline nanomembranes as thin as an atomic layer (graphene and other layer compounds) and ranging from a few nm continuously to as thick as desired (in Si and other semiconductors) are now readily available.

Graphene and sheets of other layered compounds, such as transition metal dicalchogenides or hexagonal boron nitride, which have very strong intra-layer bonding and weak bonding between layers, have electronic properties that uniquely define them, but in classical tetrahedrally bonded semiconductors, thinness in and of itself brings little new in electronic properties. When we first proposed research on Si nanomembranes, we were greeted with skepticism: “It’s just thin silicon”. What thinness does bring is a modification in effective mechanical properties, specifically flexibility or compliancy. That attribute enables access to arcuate forms and the third dimension generally [3].

Thinness also brings another feature: much greater strainability than bulk material. Strain changes the lattice constant of a crystal, and with it all the intrinsic electronic and optical properties. The critical quantity in stress or distortion, the strain energy, is proportional to the volume of material, implying that thin sheets are much easier to bend, deform, or fold without breaking than thicker materials. In particular differential strain, introduced in a variety of way [lattice mismatch, thermal-expansion coefficient differences (think bimetallic strips in thermostats), light, chemical differences, piezoelectric differences,], can lead to the self-assembly of 3D nano-objects and dynamic shape changes in them. Strain differentials in the two layers of a bi-

layer sheet, or even the two surfaces of a single-material sheet, can be significant. Probably the best example is cylindrical mesostructures of differentially strained bilayers, grown on each other

Fig. 1. A SiGe/Si bilayer microtube with a PN junction formed at the point of overlap. The tube has a diameter of $\sim 10 \mu\text{m}$. The total thickness of the bilayer is 70nm. Courtesy R. Blick.

on a sacrificial host [4]. When these bilayers are released from the host, the layers in the bilayer sheet are free to share strain and will do so by rolling or twisting, or both, depending on the shape and crystalline orientation of the sheet [1,3,5]. Figure 1 shows a simple example of a bilayer tube made of Si and SiGe sheets that at the contact point form a PN junction. This patented technology [6] has been licensed for implantable remotely programmable human pain management devices.

Shapes of much greater complexity than tubes can be created with careful patterning. Among the favorites are flower shapes in analogy with kirigami (Fig 2), which can be designed to open or close when a stimulus is supplied [7-10]. These shapes could make good microrobots [7] or microgrippers [8], and one can imagine many sensing uses [9] if the degree of opening or closing could be transmitted as a signal, optically, electrically, or magnetically. Flower-like structures could also act as nanoactuators that respond to an external stimulus. If the inside or outside of the tube is selectively chemically addressable, it can open or close as the tube finds itself in different environments that change the differential strain [10].

Even very simple 3D shapes can create unique technology if the shape is at the nanoscale and the material has the appropriate properties. For example, a ribbon of graphene formed into a sine wave structure with many periods (ranging from 50-200 nm) can act as a source of coherent radiation if the charge carrier mean free path between scatterings is large enough, something that appears to be possible with graphene. It is believed that, as the charges traverse the periodically bent conductor, they radiate, creating an effect similar to that in a free-electron laser, except in a monolayer crystalline material [11]. The wavelength of the radiation is controlled by the period of the sine wave and could be varied if the period could be dynamically changed.

A free-standing ribbon of graphene (or other NM) bent into a periodic structure is obviously not structurally stable. A slightly higher level of complexity, the integration of the “active” NM ma-

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Figure 2. Meso-kirigami of bilayer nano-membranes. Differential-strain induced self-assembly of Si/SiO₂ bilayers patterned into “flower” shapes before (top row) and after (bottom row) release and strain sharing. Courtesy V. Vasilyev and J. Reid.

terial with a compliant, but passive, host [an elastomer, such as polydimethyl siloxane (PDMS), polyimide, or a hydrogel] overcomes this limitation. The mechanical moduli of such materials are orders of magnitude smaller than those of stiff, brittle semiconductors, but the thinness of the semiconductor sheet allows the mechanical properties of the elastomer to dominate, while maintaining the crystalline integrity of the NM [12]. Depending on the goal, the elastomer can serve as a carrier for small pieces of NM that have all the electronic or optical function of their rigid counterparts [13-15] or provide local points of attachment for an extended structure [16]. The resulting flexible electronic devices serve as biomedical sensors or actuators that conform to our motion rather than constraining it when adhered to our clothes or our skins; as scaffolds for cell or tissue growth; or even as transitory, dissolvable in-situ monitors. Fantastic 3D shapes in ribbon form can be generated if the base elastomer is stretched in a controlled fashion before the active NM material is chemically attached at desired locations, and is then released. The NM will curl and bend out of the plane, following rules of mechanics as it minimizes its compressive strain [16]. One can imagine fabricating complete device structures into the active-material NM ribbon before attachment and thus having a 3D arrangement of devices. The ultimate goal is making hardware “soft” without giving up sophisticated, high-performance, and durable electronic functionalities [16,17].

Alternatively, one can use conventional lithography and the behavior of semiconductor-NM/elastomer combinations in swelling solvents to create periodic self-assembled 3D structures (Fig. 3) without a need for specialized chemical attachment points. Instead the patterning creates local stress concentrations that can be varied to create different 3D arrangements [18]. Although the shapes that can be made are not as varied as those made with ribbons, the large arrays of 3D mesostructures that can be fabricated can serve as active (i.e., containing functional electronics) semiconductor NM topologies for a host of purposes. One exciting long-range goal is neuroprosthetics, whereby a semiconductor tube or channel may potentially be made to behave like the myelin sheath of a neuron, but with sensors and stimulators fabricated in the semiconductor to probe the behavior of the neuron cell growing inside the channel. Studies using differential-strain generated microtubes have been done for several years [19-21]. The recent integration of soft substrates such as PDMS or hydrogels creates an environment very similar to that of the brain, and begins to move the idea of neuroprosthetics closer to reality [18].

Figure 3. 2D array of 3D channels of Si on PDMS, fabricated by stress concentration patterning and using the behavior of PDMS in solvents. These channels can serve as artificial myelin sheaths that integrate devices for controlling or probing neuron-cell behavior [18].

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4 The driver in the assembly of these 3D nanostructures is invariably some form of differential
5 strain. The shapes are determined by the lithographic patterning, the “cutting- out” that makes
6 the connection to kirigami; for what we have discussed so far, shape changes are continuous with
7 increasing differential strain. Completing the analogy with origami, on the other hand, requires
8 “folding” or “creasing” function in the device. Foldability is introduced via hinges that are thin-
9 ner and/or more compliant, deposited and patterned into the structure that will become the 3D
10 nano-device [8, 22-25], and actuated via differential strain, which is locally dominant at the
11 hinges. Many more shapes and expanded capabilities are possible with the judicious insertion of
12 compliant hinges.
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15 We have focused our discussion here on materials whose primary function is optical or electron-
16 ic, neglecting origami-like structures possible with other materials. In the class of materials con-
17 sidered here we can expect flexible, bendable, or foldable device architectures that are highly
18 responsive to external stimuli, with unique electronic/optical/mechanical functions, but that addi-
19 tionally repeatably reconfigure between numerous folding states as a function of the stimulus,
20 thus introducing the time dimension (“4D nano-origami”). They include sensors, electromagnet-
21 ic devices, 3D nano-optics, radiation sources at new wavelengths, and metamaterials, incorpo-
22 rated into a crystalline sheet between one and one thousand atomic layers thick. Much materials
23 research, especially on hinge materials, will be required to realize such “intelligent” nano-
24 origami devices.
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