

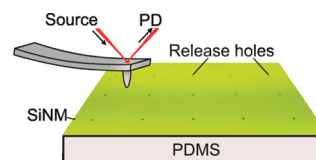
Hard Membrane, Soft Substrate

Monocrystalline semiconductor membranes bonded to soft substrates are key components of recently developed fast, flexible electronics and novel optoelectronics. The semiconductor sheet typically determines charge transport, photonic, and surface properties, whereas the soft host dominates the mechanical properties. Though such effectively compliant layered systems (ECLS) have been implemented in numerous devices and experiments, their elastic response has never been well-characterized. Little is known about how features such as the mismatch between the two materials' elastic moduli, the size of deformation, and nanomembrane thickness affect the stiffness of the layered system.

To evaluate how these factors might affect elastic response, Cavallo *et al.* (DOI:

10.1021/nn200461g) tested each one both theoretically and experimentally. First, the researchers used finite-element mechanics modeling to test the response of a Si nanomembrane ECLS with substrate elasticity between 1 kPa and 1 MPa, indented with a flat-ended cylindrical punch between 5 and 25.6 nm in diameter. The researchers found that, at large punch sizes, the layered material's elasticity was the same as the substrates'. However, with decreasing punch sizes, the model ECLS's elasticity trended toward a finite value different from the substrates' or bulk Si. Increases in nanomembrane thickness led to greater overall stiffness of the system. Testing these theoretical results experimentally, the researchers evaluated stiffness of ECLS composed of Si nano-

membranes on PDMS using indenters of various sizes, with AFM probes for the smallest ones. Results showed that the experimental findings mirrored the theoretical ones. The authors suggest that their characterization could have implications for various engineered devices based on ECLS, especially those with soft, biological substrates.

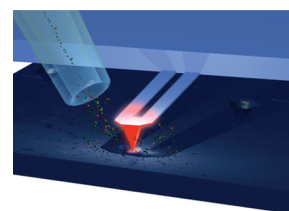


Molecular Surface Sampling Heats Up

Investigators have recently begun evaluating a novel technique known as proximal probe thermal desorption/secondary ionization mass spectrometry (TD/SI-MS), combining surface sampling at atmospheric pressure with ionization and mass spectrometric detection. This method involves placing a heated probe near or on a surface, desorbing molecular species that are then ionized and analyzed with mass spectroscopy. Early experiments with this method used probes with diameters ranging from millimeters to micrometers and lacked the ability to adjust the probe contact to the surfaces' changing topography continuously. Reducing the probe's size and incorporating real-time probe-to-surface positioning could significantly improve this technique's special resolution and chemical image quality.

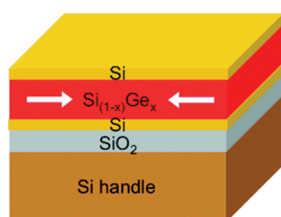
Seeking to incorporate these features into TD/SI-MS, Ovchinnikova *et al.* (DOI: 10.1021/nn200939e) looked to an atomic force microscopy (AFM) platform. With a thin film of caffeine on a glass microscope coverslip as their model, the researchers used a 30 nm diameter AFM tip heated to 350 °C to contact the film's surface. Desorbed material was then drawn into a heated transfer tube, through an electro-spray ionization region, and into the mass spectrometer. Tests showed that the probe created conical desorption craters about 250 nm across and 100 nm deep, corresponding to about 10 amol of caffeine. Mass spectroscopy readouts reliably detected caffeine. Subsequent experiments in which the probe contacted the film repeatedly, with 20 s breaks between, showed separate signals between sampling events,

negating the problem of carryover contamination. The authors suggest that this technique might be improved even further through measures currently being tested, such as heating the transfer tube to higher temperatures.



Lose the Strain, Get Defect-Free SiGe

SiGe thin films have attracted increasing attention for their promising role in quantum electronics and photonics. Depending on composition, the properties of these alloys can be continuously tuned between their two components. Though SiGe films have significant technological value, synthesizing them has proved challenging. Epitaxial growth is necessary to explore the entire compositional range of this material. However, methods developed to grow SiGe films have thus far produced materials with strain-induced crystalline defects that limit performance.



In an effort to circumvent these problems, Paskiewicz *et al.* (DOI: 10.1021/nn201547k) developed a novel method that creates defect-free SiGe nanomembranes by elastically relaxing the synthesized thin films, removing the strain responsible for defects in previously grown materials. Their new technique involves first epitaxially growing a thin layer of SiGe on silicon-on-insulator, with a buried oxide layer beneath and a Si layer above the alloy. Sandwiched between these two materials, the SiGe layer initially remains under compressive strain. Later, selectively etching away the surrounding materials frees the SiGe layer, allowing it to relax elastically and making it available for transport to other substrates. Characterization with X-ray diffraction, Raman spectroscopy, and atomic force microscopy revealed a defect-free, uniform, and elastically relaxed surface. Further

experiments confirmed the ability of the relaxed SiGe nanomembranes to act as substrates for growing defect-free strained Si layers and thick, lattice-matched SiGe. The authors suggest this method could be used to grow other crystalline materials subject to strain-related defects, including other compound semiconductor materials and complex ferroic and superconducting oxides, increasing the breadth of materials available for technologically advanced applications.

Published online July 26, 2011
10.1021/nn202443s

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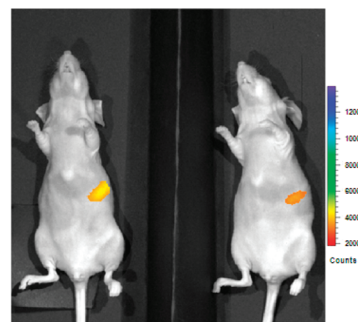
Shining a New Light on Leukemia

■ Of all the cancers, leukemia is one of the most frequent and aggressive, especially in children. In both children and adults, this disease has a high rate of multidrug resistance and relapse, with both conditions indicative of an almost certain fatal outcome. Recently, researchers identified a small population of stem-like cells present in leukemia and other cancers that seem to be responsible for resistance and relapse. Though targeting these cells could improve leukemia outcomes, finding the optimal way to do so remains a challenge.

In a new study, Barth *et al.* (DOI: 10.1021/nn2005766) showcase a new way to target leukemia stem cells directly using photodynamic therapy (PDT). This technique uses a photosensitive dye that is excited by light and transfers energy to molecular oxygen, producing highly

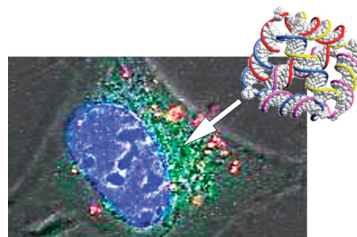
reactive singlet oxygen species that kill cells. The researchers encased their dye, indocyanine green (ICG), inside calcium phosphosilicate nanoparticles (CPSNPs), which protect the dye from degradation in plasma while also improving its photodynamic response. After tagging these ICG-CPSNPs with antibodies specific to surface features on leukemia cells, the researchers tested them in both *in vitro* and *in vivo* models of the disease. Photodynamic therapy significantly reduced viability of murine and human leukemia cell lines. In a murine model of the disease, PDT with the ICG-CPSNPs significantly extended with 29% of the treated animals having disease-free survival. The researchers suggest that ICG-CPSNPs show significant promise in treating relapsing and multi-drug-resistant leukemia, an effect

that may ultimately translate to increasing the survival rates in human patients.



Why the DNA Cage Sings

■ As researchers have become more skilled in understanding and handling DNA, they have developed the ability to assemble this genetic molecule into various useful structures, including DNA cages. This technology has rapidly progressed toward making cages of increasing complexity, ranging from simple cubes to octahedra, tetrahedra, icosahedra, and even larger structures. Preliminary studies have shown that DNA cages resist degradation by nucleases, can encapsulate proteins, and can be designed to change configuration in response to signal molecules—properties that give DNA cages the potential to act as smart vehicles for delivering therapeutics to cells. However, it has been unclear thus far whether these structures are able to enter live mammalian cells effectively.



As a proof of principle, Walsh *et al.* (DOI: 10.1021/nn2005574) created fluorescently labeled DNA tetrahedra that were shown to enter human embryonic kidney cells. After incubating plated cells with tetrahedra either alone or along with a transfection reagent, confocal microscopy and flow cytometry showed that both methods resulted in cells carrying high numbers

of tetrahedra. Förster resonance energy transfer experiments, using donor and acceptor dyes placed on different parts of individual tetrahedra, showed that the cages retained high structural integrity after they entered cells for up to 48 h. Further confocal microscopy experiments indicated that the cages were partitioned to the cytoplasm, potentially localizing to microtubule organizing centers. The authors suggest that these findings are an important proof of concept for using DNA cages as cargo delivery vehicles and controlling their actions inside cells.

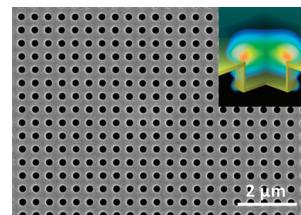
A New Order for Soft Lithography

■ Many proposed optical, photonic, and electronic applications rely on the ability to create patterned nanostructures on substrates. For example, surface plasmon resonance (SPR) sensors, a vital component in next-generation photovoltaic devices, require ordered nanostructures that cover large surface areas. Generating these nanoscale patterns reproducibly, at high fidelity, and at low cost will be key to bringing devices utilizing SPR sensors to the market. Though soft nanoimprint lithography recently generated high-quality polymer-based plasmonic crystals, this product came with a variety of drawbacks, including limited stability and refractive index range.

Seeking to improve on this latest patterning method and its resulting product, Yao *et al.* (DOI: 10.1021/nn201464t) looked to

soft embossing using inorganic spin-on-glass (SOG) materials. By pressing a PDMS stamp patterned in a photolithographic master into a SOG sol, then baking it, the researchers created an embossed layer that could be used to generate plasmonic crystals upon deposition of a thin gold film. These SOG-embossed nanostructures could further be used as durable masters to create new PDMS stamps, which could be used to mold nanostructures in photocurable materials. These SOG masters can be tuned to create reliefs of different depths by varying solvent evaporation conditions during manufacture. Tests showed that the plasmonic crystals produced by this method are highly stable even in harsh organic solvents and high temperatures and have a broad

refractive index range. The product showed utility in gas or vapor sensing and surface-enhanced Raman spectroscopy. The researchers suggest that SOG holds promise as a patterning material for generating the plasmonic crystals necessary for inexpensive, high-performance sensing devices.



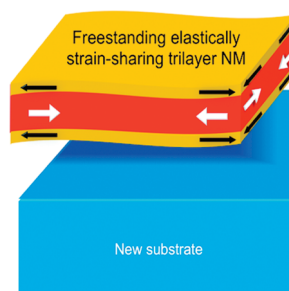
Going with the Strain

■ Researchers have long known that strain can affect a variety of crystalline materials' properties through changing the lattice constant. Being able to take advantage of this phenomenon could be a way to generate potentially useful properties that vary from that of the relaxed material. However, strain typically causes extended defects that can negatively affect material performance. Recently, crystalline nanomembranes (NMs) have provided a new option for creating strained materials. These extremely thin, flexible, and stretchable materials have already made headway in enhancing performance in semiconductors.

However, Paskiewicz *et al.* (DOI: 10.1021/nn2009672) show that these NMs can be used in an entirely new capacity by creating uniformly strained

materials that cannot be made in other ways. The researchers devised a way to create three-layer NMs with a middle strained layer, sandwiched between initially unstrained top and bottom layers that are chemically and structurally identical. After this multilayer structure separates from the substrate used to grow it, it reaches mechanical equilibrium, with strain equally shared between the three layers. This method can lead to novel materials that exhibit a strain symmetry different from that of their original, unstrained material. The researchers confirm the viability of these new materials by creating a layer of SiGe between two Si layers. While the strained middle layer would normally exhibit two-fold elastic symmetry, the trilayer system can transfer biaxially isotropic strain. The authors

suggest that this method could be used to manufacture interesting strained materials that are virtually defect-free.



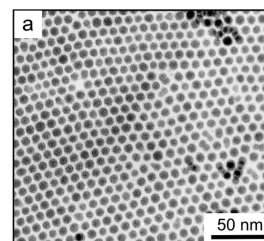
Crystallizing Our Understanding of Metallic Nanocrystals' Vibrations

■ Metallic nanoscale particles have attracted increasing attention over the past several years due to their tunable physical properties based on particle size, shape, and environment. Of particular interest are their acoustic vibrations, which have been studied through various means such as Raman scattering spectroscopy and femtosecond pump–probe spectroscopy. As manufacturing protocols have improved, researchers have developed the ability to increase the fraction of single crystalline nanoparticles. However, studies have shown conflicting results on whether crystallinity affects the fundamental radial, or breathing, mode frequency of metallic nanoparticles.

To investigate, Polli *et al.* (DOI: 10.1021/nn201468h) measured the acoustic breathing mode frequency in Co nanoparticles in both their native state and after

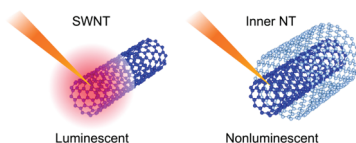
annealing, which converts the majority of these polycrystalline nanoparticles to a monocrystalline state. After synthesizing the nanocrystals in reverse micelles, the researchers heated a portion of these particles to 350 °C for several minutes, causing the structure to change from highly disordered and polycrystalline to hexagonally close-packed and single crystalline. This observation was confirmed with high-resolution transmission electron microscopy as well as the samples' low-field magnetic behavior. Using femtosecond pump–probe spectroscopy, the researchers measured the transient reflectivity signal on both the native and annealed nanocrystals, providing time-domain observation of their fundamental acoustic breathing modes and quantitative evaluation of the related vibration frequencies. Results showed only a small decrease of the breathing mode frequency in the

monocrystalline nanoparticles compared to their polycrystalline counterparts, suggesting that changes in crystallinity have little effect on breathing mode frequency. The authors suggest that these findings are in good agreement with theoretical calculations, helping to settle previous conflicting conjectures on the effects of crystallinity.



Measuring Wall-to-Wall Excitement

■ Double-walled carbon nanotubes (DWNTs), concentric tubes composed of atom-thick sheets of carbon, have attractive thermal, electronic, and optical properties that have drawn interest from both applied and theoretical researchers. Some previous studies have suggested that the inner tubes of DWNTs can photoluminesce with strengths similar to those of single-walled nanotubes (SWNTs). However, other studies suggest that photoluminescence from these inner tubes is quenched, with exciton energy passing to the outer tubes. Such exciton energy transfer between tubes could offer new and exciting research opportunities since the distance between donor and acceptor tubes is thought to be about the same as quasi-one-dimensional excitons.



To gain a better understanding of this phenomenon, Koyama *et al.* (DOI: 10.1021/nn201661q) performed femtosecond time-resolved luminescence measurements both on unpurified DWNT thin films that contain a relatively high amount of contaminating SWNTs, which can affect luminescence measurements, and films purified to increase the proportion of DWNTs. By measuring the decay time of the purified inner tubes' luminescence and

rise time of the outer tubes' luminescence, the researchers found that excitons appear to transfer between the two walls of DWNTs with a time constant of about 150 fs. This extremely fast transfer suggests that the relative intensity of the inner tubes' steady-state luminescence is nearly 700 times weaker than that of SWNTs. In contrast, the unpurified films exhibited long-lived luminescence, results expected in samples that contain high proportions of SWNTs. The authors suggest that these results provide new insight into the exciton energy-transfer rate in DWNTs, a key factor in dissecting the transfer mechanism in these unusual materials.