

Elastic strain engineering for unprecedented materials properties

Ju Li, Zhiwei Shan, and Evan Ma, Guest Editors

“Smaller is stronger.” Nanostructured materials such as thin films, nanowires, nanoparticles, bulk nanocomposites, and atomic sheets can withstand non-hydrostatic (e.g., tensile or shear) stresses up to a significant fraction of their ideal strength without inelastic relaxation by plasticity or fracture. Large elastic strains, up to ~10%, can be generated by epitaxy or by external loading on small-volume or bulk-scale nanomaterials and can be spatially homogeneous or inhomogeneous. This leads to new possibilities for tuning the physical and chemical properties of a material, such as electronic, optical, magnetic, phononic, and catalytic properties, by varying the six-dimensional elastic strain as continuous variables. By controlling the elastic strain field statically or dynamically, a much larger parameter space opens up for optimizing the functional properties of materials, which gives new meaning to Richard Feynman’s 1959 statement, “there’s plenty of room at the bottom.”

A vision of nano

At an American Physical Society meeting banquet on Dec. 29, 1959, Richard Feynman gave a talk entitled, “There’s Plenty of Room at the Bottom.”¹ He envisioned a strange future in which the entire 24 volumes of the *Encyclopedia Britannica* are written and read on the head of a pin using an electron microscope, where one makes a billion little lathes and “hands” to make still smaller lathes. Five decades later, we are well on our way to the prescient predictions of Feynman, a field now known as nanoscience and nanotechnology. Beyond mundane geometric scaling, Feynman envisioned fundamental physical and mechanical challenges and discoveries arising with miniaturization, such as problems with lubrication (“let the bearings run dry”), actuation (“internal combustion engine is impossible”), and “new kinds of effects.”

In this issue of *MRS Bulletin*, we focus on one such “new kind of effects” that has already given us better lasers, faster transistors, better catalysts, and is poised to offer much more in the foreseeable future. At its root, this effect arises out of a mantra in the mechanics of materials, “smaller is stronger,”² the science of which started in the 1950s³ and is vigorously developing today, and which Feynman could not have known about in 1959. He would be interested in its consequence: as nanomaterials are mechanically much stronger, at low temperatures at least,⁴ we can apply far greater shear or tensile stresses to tune their physicochemical properties than is

possible with traditional materials before the onset of plasticity or fracture, which relaxes the stress, elastic strain, and strain-tunable functional properties. Thus with so-called “ultra-strength materials,”² such as nanostructured silicon, pseudomorphic platinum film, and MoS₂ atomic sheet,^{5,6} we can rationally engineer the six-dimensional (6D) elastic strain ϵ_e , a continuously tunable set of variables, just like we can tune the chemical composition of a septenary alloy. The strain game would be to tune the electronic, magnetic, optical or plasmonic, ionic, phononic, thermoelectric, or catalytic properties, which is denoted as A for “any” physicochemical property or figure-of-merit, such as bandgap, carrier mobility, superconducting transition temperature, or electrocatalytic activity of a given material.

A window of opportunity has thus opened and has gotten wider over the last two decades, to a vast unexplored space for materials and device development, the size of which is probably unprecedented ever since chemical alloying was discovered. To paraphrase Feynman, there is not only room at the bottom, there is plenty of room at the bottom—by elastic strain engineering. The “room” we have in mind is the parametric space of ϵ_e , the volume of which scales as a generic deviatoric (non-hydrostatic) elastic limit ϵ_{ec} to the fifth power. ϵ_{ec} , in accordance with “smaller is stronger,”¹ scales up as $\epsilon_{ec} \propto L^{-\alpha}$, where L is a dominant characteristic length scale of the material that can be the grain size in a bulk nanocrystalline

Ju Li, Massachusetts Institute of Technology, USA; liju@mit.edu
Zhiwei Shan, Xi’an Jiaotong University, China; zwshan@mail.xjtu.edu.cn
Evan Ma, Johns Hopkins University, USA; ema@jhu.edu
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material as in the Hall-Petch relation,⁷ the thin-film thickness, or the sample size⁸, and α is an exponent,² usually between 0.5 and 1. This space of opportunity is much larger than that of high-pressure physics, which scales linearly with the pressure limit. Indeed, strain engineering (SE)—which consists of both elastic strain engineering (ESE) and inelastic strain engineering (ISE), is by definition a superset of high-pressure physics.

Material under strain

High-pressure physics has demonstrated that amazing physical properties can be achieved by stress; for example, solid sodium can be turned into an electronic insulator and become transparent to visible light⁹ by applying a large compressive stress ($\sigma_{11} = \sigma_{22} = \sigma_{33} = -P < 0$) conveyed by a pressure-transmitting fluid in a diamond anvil cell. It is well known that all properties of a crystalline material depend on its lattice parameters and the shape of the unit cell. However, it is only in the last two decades that the possibility of applying a large non-hydrostatic stress, for example a shear stress τ ($\sigma_{11} = \tau, \sigma_{22} = -\tau$), or a uniaxial tensile stress ($\sigma_{11} > 0, \sigma_{22} = \sigma_{33} = 0$), can be used experimentally to significantly alter the functional properties of a material. The main difficulty is that unlike hydrostatic pressure, both shear stress and tensile stress in materials can be relaxed by plasticity or fracture (see **Figure 1**, top right panel). Traditional materials usually cannot sustain elastic shear strain or tensile strain exceeding 0.2–0.3% before such inelastic relaxations set in. In recent years, however, a new class of materials called ultra-strength materials² has arisen, which can sustain shear or tensile strain exceeding 1% over the entire sample and for time periods sufficiently long for functional applications.

Some basic notions of mechanics of materials would be helpful for non-specialists. Strain $\boldsymbol{\varepsilon}$ is a 3×3 symmetric tensor, with six independent components. In this article, we focus on the non-hydrostatic (deviatoric) part of $\boldsymbol{\varepsilon}$, with $6 - 1 = 5$ independent components (the single hydrostatic degree of freedom is the domain of high-pressure physics). The total strain $\boldsymbol{\varepsilon}$ at a given point \mathbf{x} in the material can be decomposed into the sum of elastic strain and inelastic strain: $\boldsymbol{\varepsilon}(\mathbf{x}) \equiv \boldsymbol{\varepsilon}_e(\mathbf{x}) + \boldsymbol{\varepsilon}_i(\mathbf{x})$. $\boldsymbol{\varepsilon}_e(\mathbf{x})$ describes distortion of the Bravais lattice vectors of “good crystals” away from defect cores and can be directly measured by selected-area electron or x-ray diffractions. $\boldsymbol{\varepsilon}_i(\mathbf{x})$ corresponds to bonding topology or phase transformation changes and can be harder to experimentally quantify locally. To a good approximation, the local stress $\boldsymbol{\sigma}(\mathbf{x})$ is a function of only the local elastic strain: $\boldsymbol{\sigma}(\mathbf{x}) \approx \boldsymbol{\sigma}(\boldsymbol{\varepsilon}_e(\mathbf{x}))$. The analogy between strain field $\boldsymbol{\varepsilon}(\mathbf{x})$ and

chemical concentration field $\mathbf{c}(\mathbf{x})$ in alloys is apt, since both quantities are internally conserved and have volume integrals set by external boundary conditions (displacement and mass action, respectively). The elastic limit $\boldsymbol{\varepsilon}_{ec}$ is like the solubility limit of a single phase in chemical free energy: dumping $\boldsymbol{\varepsilon}(\mathbf{x})$ into a volume beyond $\boldsymbol{\varepsilon}_{ec}$ would cause “precipitation” of the total strain into inelastic strain $\boldsymbol{\varepsilon}_i(\mathbf{x})$, which is very large in amplitude but spatially localized^{10,11} (such as in between two adjacent atomic planes in dislocation-swept areas, where $\boldsymbol{\varepsilon}_i(\mathbf{x}) \sim 1$), plus a residual elastic strain field, which is delocalized spatially but is smaller in amplitude. In ESE, one aims to achieve an unconventionally large amplitude $\boldsymbol{\varepsilon}_e(\mathbf{x})$, which can be slowly varied in a pristine interior region to affect $A(\mathbf{x})$ of the “good crystal.”

Besides ESE, one can also engineer the inelastic strain pattern $\boldsymbol{\varepsilon}_i(\mathbf{x})$ to control properties, for example, by controlling slip or deformation twinning, martensitic phase transformation, or multiferroic domain patterns.¹² As inelastic strains are localized in microstructures such as dislocation-swept areas, new grains, or domain variants (or new martensitic phases), ISE is philosophically direct kin of “microstructure control properties,” probably the best known mantra in materials science. In certain applications, where the property of interest is phase

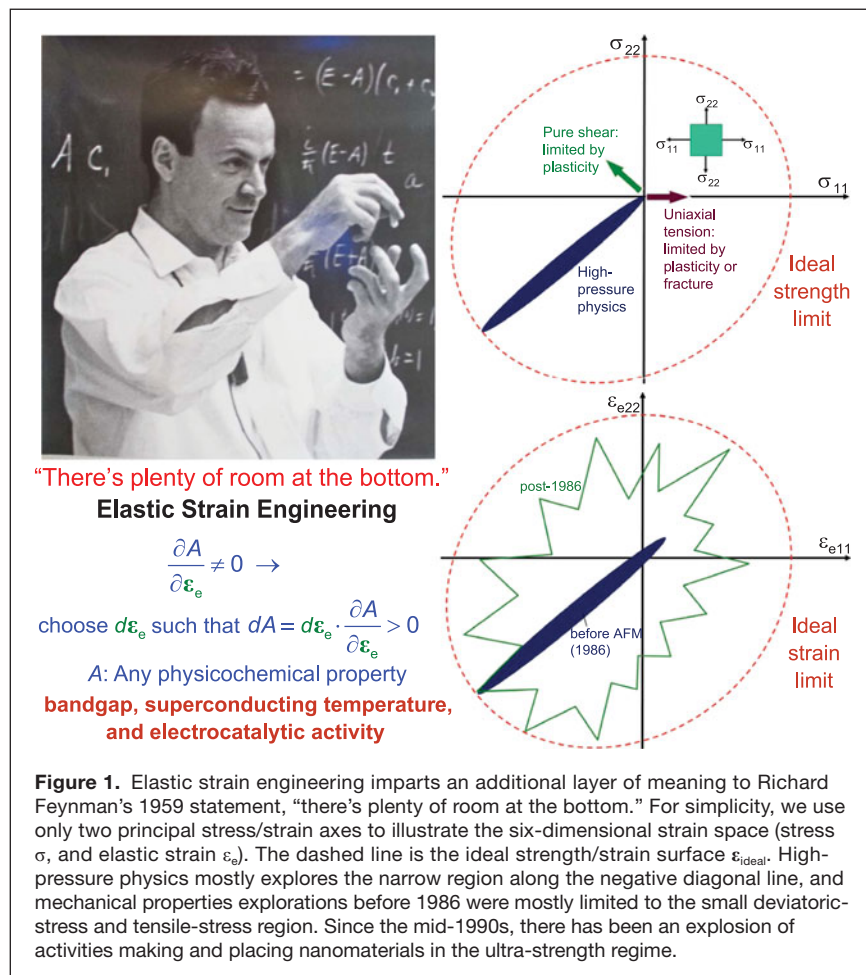


Figure 1. Elastic strain engineering imparts an additional layer of meaning to Richard Feynman’s 1959 statement, “there’s plenty of room at the bottom.” For simplicity, we use only two principal stress/strain axes to illustrate the six-dimensional strain space (stress σ , and elastic strain ε_e). The dashed line is the ideal strength/strain surface $\boldsymbol{\varepsilon}_{ideal}$. High-pressure physics mostly explores the narrow region along the negative diagonal line, and mechanical properties explorations before 1986 were mostly limited to the small deviatoric-stress and tensile-stress region. Since the mid-1990s, there has been an explosion of activities making and placing nanomaterials in the ultra-strength regime.

transformation, ESE and ISE are used in conjunction, and the entire approach is called SE. In this issue, Schlom et al. have a fascinating review on ESE and ISE of ferroic thin films. In this case, an approach is to first prepare the sample in pure ESE via epitaxial growth and elastic straining; and then for applications, to trigger multiferroic ISE transformations, whose key characteristics (such as Curie temperature) are changed by the ESE preparation in the first step. While the two effects, ESE and ISE, intimately couple in the second step, in the first step, one deals with pure ESE issues.

While microstructural/defect/domain engineering by ISE is very powerful, we focus more on the pure ESE aspects in this issue, wherein a large swath of the material is a “good crystal” and free of defects, with uniform or gradually varying $\epsilon_c(\mathbf{x})$ inside. In the context of pure ESE, microstructures (such as surfaces and grain boundaries), to the extent that they exist on the periphery, only assist in the buildup of $\sigma(\mathbf{x})$ and $\epsilon_c(\mathbf{x})$ in the defect-free interior. We study mechanisms of inelastic relaxations, but only for the purpose of defeating them. For example, one might wish to suppress dislocation nucleation and diffusional creep so one can inject and maintain a large $\epsilon_c(\mathbf{x})$, say 2% uniaxial tension along [111], in a piece of pristine silicon at 60°C for five years, which is the life expectancy of a personal computer. In the context of pure ESE, microstructural evolution is something to be avoided or suppressed, as it often leads to stress relaxation and storage of unpredictable defects in the interior, which may lead to degradation of functional properties such as carrier mobility. So the philosophy and objective of ESE are somewhat distinct from those of traditional materials processing. We note that historically, when metallurgists first described “microstructure control properties,” they had mostly mechanical properties in mind. They were not, by and large, thinking of fundamentally changing physical or chemical properties. ESE, on the other hand, aims to do exactly that. For example, through tensile straining, ESE aims to reduce the bandgap of germanium and change it from an indirect bandgap semiconductor to a direct bandgap semiconductor so it can become a better gain medium for lasers.¹³

The basic difference between “ultra-strength materials”² and conventional materials is the following. While a conventional piece of steel can easily stretch or bend by 30%, more than 99% of the injected total strain turns into plastic strain, and less than 1% of that remaining is elastic strain ϵ_c . Indeed, few conventional materials produced before 1970, whether steels or wafer-scale silicon, can withstand a sample-wide elastic strain level exceeding 1%, which is what one needs to achieve significant physical property changes. (From *ab initio* quantum mechanical calculations, we know for instance if the lattice constant of a semiconductor dilates by 1%, there can be ~100 meV change in the bandgap,⁵ which is significant).

The reason is simple. Steels have a Young’s modulus $E \sim 200$ GPa, so $\epsilon_c > 1\%$ means sustaining ~2 GPa stress sample-wide, which exceeds the yield strength of most steels. Thus, in a stress ramp-up experiment, dislocations would start to move

and multiply probably around $\epsilon_c = 0.3\%$ (if we assume a yield strength of 600 MPa), meaning we can no longer inject much more ϵ_c with further stretching or bending, while numerous dislocations start to evolve everywhere. The same is true for a bulk ingot of silicon or a silicon wafer ($E \sim 150$ GPa): $\epsilon_c > 1\%$ means sustaining 1.5 GPa tensile stress indefinitely. A 12-inch silicon wafer would fracture probably at one-tenth of that uniaxial tensile stress. Few materials produced before 1970 are therefore suitable for ESE.

ESE, as a theoretical concept, is not new, and many researchers likely have thought about it. But without real samples, ESE could not have become an experimental reality. Unbeknownst to most researchers, there were a few exceptions to this materials vacuum before 1970. Metallic whiskers grown at the General Electric Company with a smallest diameter of 1.2 μm were found to withstand several percent tensile elastic strain by Sidney S. Brenner in 1956.³ (These whiskers were the predecessors of nanowires that have been extensively studied since the late 1990s.)

Ultra-strength material is defined as being able to sustain sample-wide elastic strain levels exceeding 1% (for example, uniaxial tensile strain $\epsilon_{xx} > 1\%$ or engineering shear strain $\gamma_{xy} \equiv 2\epsilon_{xy} > 1\%$) at the service temperature of interest over anthropologically useful timescales such as months, years, or decades. The qualification of space-time volume is important: even with conventional materials, defect cores (such as at the crack tip) near the lattice can sustain very large stresses in a very local region. However, as stated earlier, in ESE, we try to avoid unintended defects and to use pristine material. Also, the qualification of service temperature is important. Ultra-strength materials are created by “going nano.” At lower temperatures, “smaller is stronger” is true for most nanomaterials due to size confinement of the dislocation population dynamics in ductile materials, or Weibull statistics of failure in brittle materials.² But when going to higher temperatures, smaller can be much weaker for nanomaterials due to the activation of diffusional creep.⁴ The transition temperature, T_{trans} , from “smaller is stronger” to “smaller is much weaker” scales with the melting point of the base material. Thus, ESE should be considered mostly for “hard nanomaterials” with relatively high melting points, for near-room-temperature applications, or below, such as superconducting cables.

The detailed reasons why nanostructured materials tend to have ultra-strength at lower temperatures, as well as the various mechanisms of stress relaxation, can be found in a comprehensive review.² A key reason is that free surfaces and grain boundaries influence the population dynamics of inelastic strain carrying defects such as glissile dislocations and cracks, driving the “smaller is stronger” trend. Size-dependent sample preparation and sample quality (initial defect densities) are also critically important.¹⁴

An ESE wonderland

Generally speaking, take any physical or chemical property A such as the thermoelectric figure of merit, ZT , the gradient

$\mathbf{g} \equiv \delta A / \delta \boldsymbol{\varepsilon}_e |_{a_0}$ is non-zero at the equilibrium lattice constant a_0 (unless A is the bulk Helmholtz free energy, per the definition of a_0). This means if we want to optimize A , the stress-free state a_0 is generally not the optimum, and by altering $\boldsymbol{\varepsilon}_e$ along $\pm \mathbf{g}$, we can achieve desired changes in A . If we want to increase A , we tweak $\boldsymbol{\varepsilon}_e$ along $+\mathbf{g}$; if we want to decrease A , we take $\boldsymbol{\varepsilon}_e$ along $-\mathbf{g}$. This amenability to tweaking, though trivial-sounding, is what historically chemical alloying gave us. In an alloy melt, the chemical composition $\mathbf{X} \equiv [X_{\text{Cu}}, X_{\text{Sn}}, X_{\text{Pb}}, \dots]$ is continuously tunable. Historically, the composition of a Chinese bronze “88.3 wt% Cu, 9.9 wt% Sn, 0.64 wt% Pb, . . .” was likely the outcome of a gradient-aided trial-and-error search, where A is a thermomechanical figure of merit, and \mathbf{X} was tweaked to see how much A changes until diminishing returns were produced (local optimum). The recipe “88.3 wt% Cu, 9.9 wt% Sn, 0.64 wt% Pb, . . .” was definitely not the outcome of *ab initio* quantum mechanical calculations or even a physical metallurgy understanding; for that we would have to wait until the end of the 20th century.

Of course, A may also “jump” sharply (instead of changing smoothly) if a first-order phase transformation is encountered upon changing \mathbf{X} , when one hits the solubility limit. So what is the maximum $\boldsymbol{\varepsilon}_e$ one can ever hope to inject into a lattice while maintaining a single-phase homogeneous (defect-free) state? The answer is $\boldsymbol{\varepsilon}_{\text{ideal}}$, the ideal strain, defined as the upper bound to how much elastic strain a perfect crystal (without defects or even surfaces) can withstand at $T = 0$ K without losing homogeneity. This can be calculated by forbidding imaginary phonon frequencies in the entire Brillouin zone,^{2,15} similar to the definition of local spinodal stability in single-phase solution (a positive-definite curvature in the free energy versus composition). Since $\boldsymbol{\varepsilon}_e$ lives in 6D space, $\boldsymbol{\varepsilon}_{\text{ideal}}$ is a 5D hypersurface, the crossing of which causes spontaneous strain localization.¹⁰ The magnitude of $\boldsymbol{\varepsilon}_{\text{ideal}}$ is generally on the order of 0.1 (Frenkel sinusoid argument),¹⁶ before the lattice spontaneously nucleates dislocations, cracks, or phase transforms, even at zero temperature.^{10,12} Thus, ultra-strength materials, defined as taking up more than 1% elastic strain, would be carrying more than one-tenth the theoretical ideal strength.

Note that $\boldsymbol{\varepsilon}_{\text{ideal}}$ is a concept, computable for an imagined perfect lattice under a periodic boundary condition at 0 K, whereas ultra-strength refers to an experimental reality about a real material at a finite temperature and with a significant space-time volume. Since “smaller is stronger,” the low-temperature strength champion, not surprisingly, is graphene, which has zero thickness in the z direction in the nuclei positions. A graphene monolayer experimentally demonstrated about a ~20% equal biaxial tensile elastic strain limit,¹⁷ in agreement with predictions of soft phonons by *ab initio* density functional perturbation theory (DFPT) calculations.¹⁵ Thus, the fact that ideal strain $\boldsymbol{\varepsilon}_{\text{ideal}}$ can be closely approached experimentally has been demonstrated.¹⁸

The late John J. Gilman, a giant in the field of mechanics of materials, wrote a book, *Electronic Basis of the Strength of Materials* (Cambridge University Press, 2008), in which he

explained the innate connection between ideal strength—the point where bond breaking or bond switching has to happen spontaneously—and dramatic electronic-structure changes, such as closure of the bandgap in semiconductors. Since nearly all physical and chemical properties of a material depend on the electronic structure, and since the electronic structure must be altered in a drastic way near the point of spontaneous bond breaking, a material near the ideal-strain surface $\boldsymbol{\varepsilon}_{\text{ideal}}$ will have unusual or even singular physical and chemical properties that are dramatically different from those of the stress-free state.

This has been demonstrated in the DFPT calculations for graphene:¹⁵ In the stress-free state, graphene has an $\omega \propto k^2$ bending phonon branch in the phonon dispersion curve (for angular frequency ω and wave number k); with tensile strain, the $\omega \propto k^2$ branch disappeared. When strain is increased further, a wide phononic bandgap opens up, which never existed in stress-free graphene. The 15%-stretched graphene is therefore a very different material from 1%-stretched graphene, phononically. Because the thermoelectric effect depends on phonon transport, and the Bardeen–Cooper–Schrieffer theory of superconductivity depends on electron-phonon coupling, dramatic changes in phonon dispersion may lead to dramatic changes in ZT , or the superconducting temperature T_c . In the same sense, 3%-strained germanium is unlike normal germanium,¹³ and 5%-strained germanium would also be different from 3%-strained germanium. Five percent stretched germanium is also different from 5%-sheared germanium.

In crystals, not only do the elementary-excitation (e.g., electron, phonon, magnon) bands shift in value with strain, they also change from $\omega \propto k^2$ dispersion to $\omega \propto |k|$ dispersion, or in the topology of which band branch is higher and which band branch is lower (band inversions). It is thus not surprising that even the “fragility” or robustness of topological insulators is proposed to be classified by how much elastic strain they can sustain before their topological non-trivialness (genus of band topology) changes.¹⁹ ESE not only has the ability to change values of properties, it can also push chemical and physical behavior toward singularities and induce topological changes, creating an ESE wonderland. This wonderland has been in the heads of theorists for a long time. But now, it is well poised to become an experimental reality in many materials subfields.

For monolayers such as graphene and MoS₂, as well as van der Waals heterostructures,⁶ the three in-plane strain components ε_{xx} , ε_{yy} , and ε_{xy} should be treated differently from the out-of-plane deformation characteristics. One may say that a true monolayer like graphene does not have out-of-plane strain, but in that case, due to the ease of bending, one must also consider the influence of elastic bending (3 degrees of freedom, the two principal bending curvature values plus the angle of one principal axis) on local physicochemical properties, which is a limiting case of the more general “flexoelectric” (“strain gradient $\nabla \boldsymbol{\varepsilon}_e$ ”) effect.²⁰ Furthermore, there are atomic coordinates’ “internal shuffling” degrees of freedom that may be exploited in MoS₂ and van der Waals heterostructures,⁶ so

the ESE wonderland of 2D materials is no less rich and exotic than that of 3D materials.

Recently, meticulously designed artificial “metamaterials” and origami materials have attracted much interest, with intended applications as photonic crystals, plasmonics, etc. When these materials are made of elastomers, or have bending/folding based architecture, they tend to be highly deformable in a reconfigurable manner (e.g., “mechanical metamaterials”) and therefore also provide a playground for ESE and ISE²¹ of photonic and phononic properties, for example.

Four pillars of ESE

ESE has one gigantic commercial success already that can serve as its poster child: strained silicon technology, where biaxial or uniaxial tensile strain up to a few percent is applied to a 10¹–10² nm wide silicon channel (by epitaxial strain to Si_{1-x}Ge_x substrate for example) to achieve dramatic acceleration in carrier mobility by up to a few hundred percent. The physics behind mobility enhancement is attributed mainly to the reduction of the effective mass of electron or hole carriers and band degeneracy lifting, which can be modeled by *ab initio* band structure calculations. This piezoresistance effect²² has been demonstrated for a long time. The physics is relatively straightforward. But achieving and sustaining $\epsilon_c > 1\%$ reliably in silicon in hundreds of millions of transistors for five years in real life, which is what is needed for computers and smartphones, is a great achievement of materials science and engineering. Note that the main reason silicon can take up a few percent tensile strain, without fracturing, is because it is in the form of a nanochannel (“small-volume material”) and not as a whole wafer.

The concept of strained silicon technology was revived at the Massachusetts Institute of Technology and Stanford University in the early 1990s, and IBM and Intel achieved major commercial successes in the mid-2000s, creating billions of dollars of added value every year. For the last decade, strained silicon technology has been one of the main contributors to so-called “non-classical scaling,” delaying the eventual breakdown of Moore’s law. In the article by Bedell et al. in this issue, this industrial technology is reviewed in detail. Strained semiconductors have also found commercial applications in quantum well lasers, light-emitting diodes, and many other optoelectronic applications.

Still, ESE is relatively obscure today, if compared with what high school students know about what chemical metallurgy has done for human civilization (Bronze Age, Iron Age). Why is this the case? As shown in **Figure 2**, ESE requires four general ingredients or pillars: (1) synthesizing nanomaterials, (2) applying force at the nanoscale and measuring physical and chemical effects, by lab-on-a-chip for instance, (3) characterizing elastic strain distribution and deformation mechanisms, and (4) accurate *ab initio* modeling of strain effects on physicochemical properties and ideal strain. Some of these four ingredients did not exist before 1980, and their grand confluence started only in the late 1990s.

First, ESE requires nanomaterials that can take a large dynamic range of elastic strain. Carbon nanotubes were identified in 1991. Bulk nanocrystals were popularized in the mid-1990s. Without these advances in synthesis, and the explosive proliferation of nanomaterials today, ESE could not have taken off.

Second, for discovery-style exploration of the large parametric space of strain, one needs “hands” to apply forces at the nanoscale. Binnig and Rohrer received their Nobel Prize in Physics in 1986 for invention of the scanning tunneling microscope, which led Binnig, Quate, and Gerber to invent the atomic force microscope (AFM) also in 1986. We can use 1986 as a landmark in nanoscience and nanotechnology. After 1986, with subsequent development of instrumented nanoindentation²³ and MEMS/NEMS, the ability of humans to impose force and strain on materials at will at the nanoscale was greatly enhanced. To directly measure physical and chemical property changes at small scales, we also need to greatly advance lab-on-a-chip and MEMS/NEMS technologies. In the future, we probably need “a hundred tiny hands” (actuators) that Feynman envisioned and an equal number of sensors for local ESE measurements *in situ*.

Third, to experimentally measure the actual elastic strain distribution inside a functional material requires high-resolution microscopy and spectroscopy,²⁴ which have been continuously developing at stunning speed (see article by Hytch and Minor in this issue). If the intended elastic strain relaxes prematurely, one would also want to probe the mechanisms of stress relaxation (dislocation slip, diffusion, fracture, etc.) and methods to defeat them. These involve the development of both long-timescale modeling^{25,26} and *in situ* microscopy^{4,12,27,28} techniques for deformation mechanism studies.

Fourth, we are no longer in the Stone Age and need to go beyond trial-and-error approaches used by our ancestors for developing chemical metallurgy. The strain space is large and easy to get lost in, so we need theory and calculations to guide us toward the upper bound to elastic strain¹⁵ and

Four Pillars of Elastic Strain Engineering

<p>1. Synthesizing Load-bearing Nanostructures</p> <p>Carbon nanotube: 1991 Graphene: 2004 Bulk nanocrystals: mid-1990s</p>	<p>2. Applying Force and Measuring Physical and Chemical Effects at the Nanoscale</p> <p>Atomic force microscope (1986) Nanoindentation Lab-on-a-chip, MEMS/NEMS</p>
<p>3. Measuring Strain and Probing Inelastic Relaxation Mechanisms at the Nanoscale</p> <p><i>In situ</i> transmission electron microscopy X-ray and electron tomography synchrotron</p>	<p>4. <i>Ab initio</i> Prediction of Strain Effect on Physico-Chemical Properties and Ideal Strain</p> <p>Density functional theory Excited-state methods (GW, BSE) Data mining</p>

Figure 2. Four ingredients of elastic strain engineering must converge for explosive growth of this field.

how much change in properties^{5,29} can be induced by strain. High-powered *ab initio* calculations, including both electronic ground-state and excited-state calculations,⁵ are crucially needed. This closely matches the philosophy behind the Materials Genome Initiative, which proposes accelerating materials discovery and development by computation and data mining.

Explosive growth of ESE requires careful and meticulous experiments, from synthesis to applying load, to characterizing strain distribution, to local property measurements and diagnostics. The agreement between theoretical predictions and measurements also builds confidence. The grand confluence of trends in the four pillars only started in the last two decades or so, and is accelerating rapidly today. In view of the long timescale our ancestors took to figure out chemical metallurgy, two decades is a just a blip on the time axis, and there is already a billion-dollar strained semiconductor industry to show for it. In view of the extraordinary number of properties elastic strain could affect, we are just getting started in our exploitations of ESE.

Recent progress

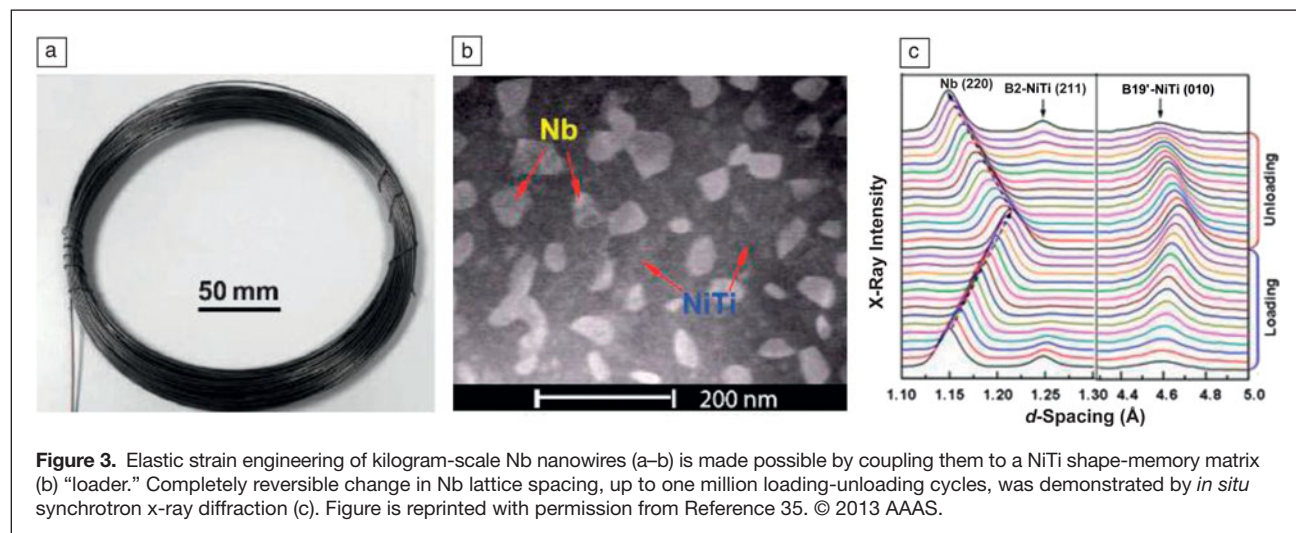
The first general symposium on ESE was held as part of the 2013 MRS Fall Meeting. The main purpose of this symposium was to (a) cross-link different materials communities: strained oxides, strained atomic sheets, strained catalysts, strained silicon technology, and nanomechanics, and (b) to delineate common toolkits (such as theory and modeling, lab-on-a-chip, and nanoelectromechanical systems) and roadmaps for rational ESE. The interdisciplinary and cross-materials-classes natures of the symposium were evident.

This issue of *MRS Bulletin* contains contributions from five invited speakers of the symposium, bringing together different communities that use elastic strain to control functional properties, from strained silicon technology (see article by Bedell et al.) that is already at the industrial scale, to strain effects on chemical kinetics, including ionic conductors and catalysts (see article by Yildiz), strained ferroic films for tuning phase

transformations (see article by Schlom et al.), and strained atomic sheets and nanowires for novel optoelectronic effects (see article by Yu et al.). The experimental and theoretical toolkits for ESE are highlighted, such as precisely measuring large elastic strain fields by microscopy (see article by Hÿtch and Minor) and spectroscopy, generating strain and measuring properties *in situ* by lab-on-a-chip and MEMS/NEMS, predicting what strain will do to physical and chemical properties (*ab initio* to continuum scale modeling), and monitoring as well as understanding how large an elastic strain can be sustained and for how long (deformation mechanisms, defect evolution, and failure in ultra-strength materials).

New applications of ESE are constantly emerging. While most of the ESE applications thus far use static, uniform elastic strain, one example of non-uniform ESE is to make strain-engineered atomic sheets as a broad-spectrum solar energy funnel. An atomic monolayer of MoS₂ can be stretched to 11% experimentally.³⁰ First-principles calculations show that monolayer MoS₂ has a tunable bandgap from 1.9 to 1.1 eV when the tensile biaxial elastic strain increases from 0% to 9%. A novel design for photovoltaic devices was proposed,⁵ where inhomogeneous elastic strain is imposed on a mechanically clamped 2D membrane. Force balance requires the local strain to scale like $1/r$ (where r is distance to the indenter) for circular geometry. Since the bandgap changes approximately linearly with the local strain, this imposes a $1/r$ like deformation potential on electron and hole carriers, creating an “artificial atom,” but in 2D.

The $1/r$ field leads to novel effects for both photon absorption and exciton transport. First, the spatially varying bandgap enables it to absorb a broad spectrum of solar photons. Second, like a funnel, the $1/r$ deformation potential induces ballistic motion of neutral excitons toward the center and thus reduces recombination probability. Third, at the “nucleus” of the artificial atom, two nano-electrodes with different work functions are envisioned to separate the exciton, thus the charge-separation region will be distinct and can be much smaller



than the photon-absorption region of the device. Calculations of the exciton lifetime and mobility indicate the photon-absorption “umbrella” can be up to microns in diameter. This strain-induced exciton funneling effect has been recently verified experimentally,^{31,32} and the same effect in elastically deformed nanowires was also demonstrated.^{33,34} (see article in this issue by Yu et al.).

While functional applications such as logic, sensing, and computing may require only a small total mass of active materials, applications such as ionic conduction and superconducting cables may require bulk-scale ultra-strength materials. Freestanding nanotubes and nanowires have ultrahigh elastic strain limits (4 to 7%) and yield strengths, but exploiting their intrinsic mechanical properties in bulk nanocomposites has historically proven to be challenging. Recently, the superior elastic limits of nanowires were shown³⁵ to be preserved in a phase-transforming matrix (**Figure 3**) based on the concept of elastic and transformation strain matching (ESE+ISE). By engineering the microstructure and residual stress to couple the true elasticity of Nb nanowires with the pseudoelasticity of a NiTi shape-memory alloy, a nanocomposite that possesses a large quasi-linear elastic strain of over 6%, a low Young’s modulus of ~28 GPa, and a high yield strength of ~1.65 GPa has been developed.³⁵ As verified by *in situ* synchrotron diffraction (see **Figure 3c**), one is able to, for the first time, stretch kilogram-scale nanowires to 6% elastic strain reversibly.³⁵ This strain-matching approach opens new avenues for developing bulk functional nanocomposites by coupling a shape-memory alloy “loader” with 0D, 1D, and 2D nanoscale components for ESE of kilogram-scale active materials, based on the observation that the true elastic strain range of many nanoscale objects (e.g., nanotubes, nanowires, quantum dots, graphene) happens to match the pseudoelasticity strain range of many shape-memory alloys. This may find applications in enhancing ion transport and catalysis (see article by Yildiz), thermoelectric energy harvesting, and superconductivity by ESE.

Conclusion

Considering what chemical alloying has accomplished for human civilization, the long-term possibilities for elastic strain engineering (ESE) are mind boggling. The much larger dynamic range of deviatoric elastic strains that nanomaterials can sustain over months and years, which can be tensile in character, leads to the “new kinds of effects” that Feynman envisioned. The explosive growth and timely confluence of the four ingredients needed for ESE—(1) synthesizing nanomaterials, (2) applying force at nanoscale and measuring physical and chemical effects, (3) characterizing elastic strain distribution and strain relaxation mechanisms, and (4) accurate *ab initio* modeling of strain effects on physicochemical properties—in

the past two decades and the significant commercial success of strained semiconductors technology suggest that we are just getting started in reaping tremendous benefits from ESE.

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