NANOMECHANICS

Full recovery takes time

On bending, nanowires display anelastic behaviour, recovering their initial shape over time and efficiently dissipating mechanical energy in the process.

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With the advent of near-equilibrium growth techniques, it is now possible to synthesize virtually any type of crystalline nanostructure. Researchers can exert a fine control over size, shape and surface chemistry to tailor the properties of their nanomaterial to specific applications relevant to energy conversion, sensing, electronics and photonics. Once in a device, these nanostructures are frequently subjected to intense mechanical duress, so structural integrity becomes a key factor for ensuring robust performance. Unfortunately, the mechanisms that govern irreversible deformation and, ultimately, failure of nanomaterials are a far cry from the mechanisms at play in their bulk counterpart and are still largely unclear. Writing in *Nature Nanotechnology*, Yong Zhu, Huajian Gao and collaborators from North Carolina State University and Brown University now report another remarkable behaviour of nanoscale materials, showing that seemingly irreversible, plastic deformations in ZnO and p-doped Si nanowires can gradually recover over time[1]. The ability of a material to recover plastic deformations in a measurable timescale is called anelasticity and it is usually very small in bulk inorganic materials at room temperature.

Two notable characteristics that affect the mechanical properties of nanoscale materials underpin the profound difference with their bulk counterpart: the prevalent role of surface and near-surface regions and the scarcity of defects (high crystalline quality).

In the case of an elastic strain imposed on a material, for example, deformation is entirely reversible. However, nanomaterials can exhibit different elastic moduli, mainly because surface atoms have truncated chemical coordination therefore possessing a unique electronic structure, which make them prone to relaxation and reconstruction dynamics. At vanishingly small length scales, the unique mechanical properties of the surface layer tend to dominate the total elastic response of the material[2]. Depending on the nature of the surface stiffness and the surface stress state, nanowires may exhibit either size-dependent elastic stiffening or softening[3,4].

Once the elastic limit is reached, a material without the capacity to sustain plastic deformations fractures in a brittle fashion under an applied load. But if the material has the intrinsic ability to sustain plasticity, specific mechanisms that can cope with very high stresses come into play[5]. Dislocations — quasi-1D defects delineating slipped and unslipped regions of a crystal — are the vehicles for plastic deformation in bulk materials. However, nanomaterials synthesized by bottom-up techniques contain a paucity of dislocations[6] and thus nucleation of new defects is needed to commence plastic deformation. Stress-driven nucleation requires subjecting a nanomaterial to stresses approaching the theoretical strength for perfect crystals (often more than 1,000 times greater than bulk strengths). In these extreme conditions and at the reduced length scales of a nanomaterial, conventional plasticity mechanisms have been shown to give way to atomic diffusion[7–9]. As a thermally activated mechanism, atomic diffusion is expected to give rise to a time-dependent mechanical response and provide dissipative channels that can gradually relax plastic strains; yet, if stresses are spatially uniform, diffusion-mediated anelasticity should be negligibly small.

The work by Zhu and colleagues experimentally demonstrates that a spatially varying strain field (in the form of bent nanowires) can accelerate diffusion of point defects, giving rise to both permanent deformation and a gradual recovery of a large portion of the plastic strain on removing the load (Fig. 1a). The researchers used microelectromechanical actuators to deform individual ZnO and p-type Si nanowires, and measured the resulting strain over a timescale of tens of minutes. For both materials, they observe an anelastic recovery that is proportional to the amount of imposed strain and the holding time at the peak loading. The bending creates a high stress gradient across the nanowire width that is inversely proportional to its radius (Fig. 1b). In a short space, therefore, the axial stress goes from tensile (on the external surface)

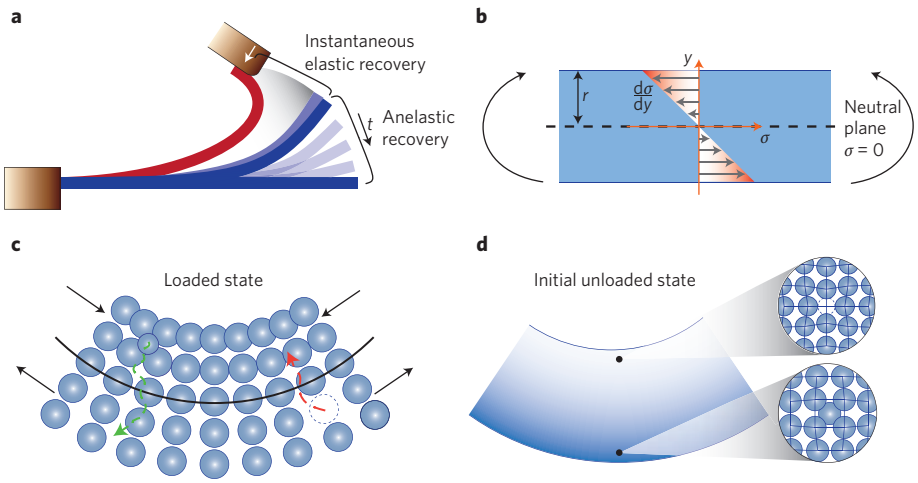

Figure 1 | Anelastic (time-dependent) strain recovery in bent inorganic nanowires. **a**, Cartoon depiction of single nanowire bending experiments[1]. On releasing the load applied by a nanomanipulator, an instantaneous elastic recovery ensues, followed by a slower anelastic recovery leading to nearly full shape recovery over time, *t*. **b**,**c**, The presence of large stress gradients $d\sigma/dy$ that scale inversely with the nanowire radius *r* provides a large driving force for diffusion of point defects (vacancies and interstitial atoms; trajectories shown by red and green arrows, respectively). **d**, After the initial elastic recovery, point defects are no longer spatially uniform and disturb the otherwise perfect lattice. Shape recovery is caused by the redistribution of these point defects over time.

to compressive (on the internal surface), leading to a sharp chemical potential gradient across the width of the nanowire that drives a pronounced anelastic response (Fig. 1c). Interstitial point defects prefer to reside at tensile regions, whereas vacancies can be accommodated at compressive regions (Fig. 1d). Using electron energy-loss spectroscopy, the researchers measure a chemical shift moving from one side to the other in the bent ZnO nanowire, with oxygen enrichment emerging in tensile regions. This suggests that the mechanism for the anelastic relaxation involves oxygen atoms as the mobile species. Zhu and colleagues quantitatively model these observations using a Gorsky-type relaxation, a mechanism in which point defects distort the lattice and have sufficiently high mobility to diffuse.

Several questions remain open following these findings. For instance, what are the detailed diffusion pathways for the initial plastic deformation and the ensuing anelastic relaxation, particularly in cases where multiple atomic species are involved? Do the surface atoms mediate diffusion along the width of the nanowires, and how facile is such a process for the various inorganic species? Given the competing time constants associated with relaxation and diffusion, would the anelastic response be size-dependent? Does the introduction of internal sinks for point defects — such as a grain or interphase boundary — shut off the anelastic behaviour?

Even with these questions still to be answered, anelastic relaxation provides a new — and surprising — means for shape recovery of nanoscale materials. A notable upshot of the work of Zhu and colleagues concerns the application of these nanomaterials for mechanical energy dissipation. To this end, the ZnO nanowires tested by the researchers already surpass typical bulk materials such as Cu–Mn alloys by twofold[10]. ❐

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Correction

In the version of the News & Views article 'Bioelectronics: Injection and unfolding' originally published (*Nature Nanotech.* **10,** 570–571; 2015), in ref. 5, the page number range was incorrect. Corrected in the online versions after print 3 July 2015.

Correction

In the version of the Commentary 'Memory leads the way to better computing' originally published (*Nature Nanotech.* **10,** 191–194; 2015), in Fig. 2 all data for STT-MRAM were too low by a factor of 10, and the lowermost data point for RRAM was a miscalculation of the original data in A. Chen, *et al. IEDM* 746–749 (2005); it should have appeared at 900 nm^2, 12 pJ. Corrected in the online versions 8 July 2015.