Atomistic Perspective on In Situ Nanomechanics

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ABSTRACT

Nanostructured materials exhibit superior physical and mechanical properties, and they hold great promise for enabling the development of novel micro/nano electro-mechanical systems. A fundamental understanding of the mechanical deformation and degradation in nanostructured materials is critical for designing the damage-tolerant nanostructures and devices. The *in situ* transmission electron microscopy provides a novel approach to uncover the dynamic deformation mechanisms in nanostructured materials, especially at the atomic scale. This review presents an overview of recent progress in the atomic-scale study of mechanical properties, dynamic deformation and degradation in a variety of nanostructured materials. Experimental techniques for *in situ* nanomechanical testing are reviewed. New insights into the atomic-level mechanical behavior of nanostructured materials are described, including surface-mediated defect processes, size-dependent deformation mechanisms, plastic deformation of nanotwinned and nanocrystalline materials, phase transformation, liquid-like behavior and pseudoelasticity, bending and fatigue, *etc.* Future research on the *in situ* nanomechanics is also discussed. Ultimately, the *in situ* nanomechanics study will enable a complete understanding of the atomic-scale dynamic deformation, thereby providing a mechanistic basis of the rational design and fabrication of durable nanomaterials and nanodevices.

Key words: *In situ* transmission electron microscopy; nanomechanics; atomic scale; nanostructured materials.

1. Introduction

Nanostructured materials possess excellent mechanical properties such as ultrahigh strength, large elastic strain limit and high deformation reversibility. They hold great promise for enabling the development of novel micro/nano electro-mechanical systems (MEMS/NEMS)¹⁻⁵. The unique mechanical properties of nanostructured materials are also of technological importance for tuning their physical-chemical properties, such as band gap, electronic conductivity and catalytic performance, by the applied strain field^{1,6,7}. However, mechanical degradation occurred frequently in nanostructured materials under mechanical loads, resulting in a loss of structural stability, as well as a compromise of functional properties^{4,5}. Therefore, a fundamental understanding of the mechanical behavior of nanostructured materials, especially at the atomic scale, plays a key role in the development of damage-tolerant nanomaterials and devices.

Molecular dynamics (MD) simulations^{2,8-11} have provided mechanistic insights into the atomic-scale mechanical behavior of nanostructured materials. They are, however, limited by the high strain rate, approximate nature of interatomic potential, small system size and idealized crystal structure. There is currently a critical need of validating the discoveries from MD simulations by nanomechanical experiments. Recent development of nanofabrication and nanomanipulation technologies allows us to precisely handle and load the nano-sized samples¹²⁻¹⁵. More importantly, the *in situ* transmission electron microscopy (TEM) provides a powerful approach to directly visualize the dynamic material processes at the atomic scale¹⁶⁻²⁰. This review presents an overview of recent progress in the atomistic study of the dynamic deformation and degradation in nanostructured materials. We will first review the novel experimental

techniques that enable *in situ* TEM nanomechanical testing. Then the atomistic mechanical behavior of nanostructured materials will be described, including surface-mediated defect processes, size-dependent deformation mechanisms, plastic deformation of nanotwinned and nanocrystalline materials, phase transformation, liquid-like behavior and pseudoelasticity, bending and fatigue, *etc.* Future research of *in situ* nanomechanics will be discussed, with an emphasis on the development of the *in situ* nanomechanical testing under high resolution TEM (HRTEM).

2. *In situ* atomic-scale nanomechanical testing

Past decade has witnessed a significant increase of the *in situ* nanomechanical testing of nanostructured materials. *In situ* straining has been realized in various characterization platforms, including atomic force microscopy (AFM)^{21,22}, scanning electron microscopy¹⁴, TEM^{16,17,23,24}, neutrons and X-rays diffractions²⁵ *etc.* Among these advances, *in situ* TEM nanomechanical testing so far provides the most direct means of atomic-scale structural characterization and strain analysis^{16,19}. The protocols for TEM-based nanomechanical testing have been extensively reviewed in recent publications^{16,17,19,20,26}. Here, we focus on a novel probe-based *in situ* TEM method that has enabled the nanoscale sample fabrication, manipulation and mechanical testing.

In situ TEM nanomechanical testing was critically hindered by the difficulties of sample clamping and straining. Thin film samples are usually adopted in the traditional single-tilt TEM straining stage, in which the sample geometry and force are difficult to determine^{17,19,27}. Recently, nanoindentation, AFM, MEMS-based testing device and scanning tunneling microscope (STM) probe were incorporated into the TEM platform^{16,17,23,24,28}. *In situ* mechanical testing via nanoindentation, AFM and MEMS

device have revealed a number of novel deformation phenomena and size-dependent responses in nanostructures, which were typically synthesized by a chemical method or fabricated by focused ion beam (FIB) cutting^{29,30,31}. However, large samples (>100 nm) were usually employed in the *in situ* TEM straining with nanoindentation, AFM and MEMS device. In addition, it was hard to conduct the high-quality atomic imaging due to the difficulties of varying the sample orientation. Moreover, material damages generated during the FIB fabrication or device assembly could affect the intrinsic deformation responses of nanostructures.

The probe-based technique enables us to effectively manipulate and strain the nanostructures with different sizes (from few nanometers^{32,33} to submicron scale³⁴) and geometries (*e.g.*, nanowire³⁵, nanoparticle^{32,33}, nanopillar³⁶ and thin film³⁷) with the atomic resolution. Typically, a metal rod with nanosized samples is used as one end of the TEM stage, and a STM probe driven by a piezo-controller serves as the other end of the stage (Figure 1a). Before straining, the connection between sample and STM probe can be made easily inside a TEM, via cold welding¹², potential-induced welding¹³ or amorphous carbon deposition³⁴. Moreover, the crystal orientation is tunable via a slight bending of sample side, thus facilitating the *in situ* atomic-scale imaging. Besides, a nanoindenter or AFM cantilever can be further incorporated into the TEM stage in an alternative setup for stress-strain measurements^{35,38}. High-temperature nanomechanical testing could also be realized in the probe-based method, via the Joule heating through a control of electric current²⁸. As a result, it became feasible to perform a systematic investigation on the atomic-scale structure-property-deformation relationship in nanostructured materials.

Figure 1. *In situ* TEM experimental setup for the probe-based nanomechanical testing. (a) The TEM-STMM platform. (b) A bulk W rod with nanoscale surface edges. Scale bar, 100 nm. (c) The W probe was driven to contact with a nanoedge, and a 3 V potential was pre-applied on the W probe. Scale bar, 200 nm. (d) A W nanowire formed when the contact between the W probe and a nanoscale edge was made. Scale bar, 5 nm. Reprinted with permission from Ref. 13¹³. © 2015 Nature Publishing Group.

The probe-based technique also enables the nanoscale sample fabrication and device assembly. For example, two pre-existed nanostructures can be cold-welded when they are put into contact, thus creating a new nanosized sample^{12,32}. However, this method only works to make the nanosized face-centered cubic (FCC) metals. Recently, Wang *et al.*^{13,39} further developed an *in situ* thermal welding technique to fabricate the high-quality metallic nanostructures directly inside the TEM (Figure 1b-d). Specifically, a small voltage potential is pre-applied on either side of the sample stage. A nanowire with uniform geometry can be fabricated via a localized melting-quenching process, when the STM probe contacts with a nanoscale edge on the fractured surface of a bulk

metal rod (Figure 1d). *In situ* tension or compression testing can be subsequently conducted on the as-fabricated nanowire with atomic-scale resolution. More importantly, this *in situ* welding method is generally applicable to a variety of material systems, such as FCC and body-centered cubic (BCC) metals¹³, and metallic glasses⁴⁰. Usually, clean sub-100 nm samples are obtained after welding, in contrast to the commonly-used FIB cutting which often produced large samples (>100 nm) with surface damages¹³. *In situ* welding also enables the controlled fabrication of nanostructures (including single-crystal, bicrystal or nanotwinned samples), with different sizes (from several nanometers to ~100 nanometers) and orientations¹³. Such a facile fabrication technique enables the systematic study of various material and geometrical factors that influence the deformation of nanostructured materials.

3. Surface-mediated defect nucleation

The mechanical properties and deformation of nanomaterials can be strongly influenced by sample size^{14,41}. Uchic *et al.*¹⁴ measured the size-dependent strengthening responses in micron-sized metal pillars. Such a sample size effect was attributed to the source-controlled dislocation plasticity^{29,30,41}. In small crystals, mobile dislocations can easily escape from the free surface before having a chance to multiply, resulting in the starvation of dislocation inside the small volume. As a result, higher stress is required for the nucleation of new dislocations for further deformation^{41,42}. This has been confirmed by Shan *et al.*³⁰ who showed that under *in situ* TEM compression, the sub-micron Ni crystals with preexisting defects were mechanically annealed to a dislocation-free state; and further plastic deformation was constrained by the dislocation nucleation sources³⁰. However, due to the lack of traditional sources (*e.g.*, the Frank-Read sources), new

dislocation sources have to be triggered in the small volume. In the micron and sub-micron sized FCC and BCC single crystals, single-arm dislocation sources were found to operate so as to control the dislocation nucleation, as revealed by Oh *et al.*²⁹, Kiener *et al.*⁴³, Mompoua *et al.*⁴⁴ and Chisholm *et al.*⁴⁵. Dislocations emitted from the single-ended sources quickly escaped from the crystal before being able to multiply. The exhaustion of both dislocations and dislocation sources increased the deformation stress, contributing to the size-dependent strengthening.

Figure 2 Surface-mediated dislocation nucleation in metallic nanowires. (a-c) Surface nucleation of dislocation in a FCC Au nanowire. Insets in a and b are the Fourier-filtered images, showing the nucleation process. Scale bars, 3 nm. (d-f) Dynamic dislocation processes in a BCC W nanowire under [112] compression, exhibiting the formation and expansion of dislocation dipoles. Scale bars in (d-e), 5 nm; (f-g), 2 nm. Reprinted with permission from Ref.32³² and Ref.13¹³. © 2015 Nature Publishing Group.

As the crystal dimension further decreases, the free surface is believed to serve as the dominant dislocation sources and annihilation sites in controlling the plasticity and size-dependent strengthening^{2,11,46,47}. Zheng *et al.*³² reported the first surface-controlled dislocation nucleation and annihilation in sub-10 nm FCC Au nanowires (Figure 2a-c). Under mechanical loading, the elastic strain concentration can be readily built up at the surface steps of Au nanowires. Above a critical load, a leading partial dislocation, with a stacking fault (SF) behind, was observed to emit from the surface, presumably from a favorable surface step (Figure 2b), thereby releasing the lattice strain. Subsequently, a trailing partial nucleated and then eliminated the SF. The resulting full dislocation glided within the nanowire and finally escaped from the opposite surface, inducing the annihilation of a surface-nucleated dislocation. As a result, further deformation was controlled by the discrete nucleation events of partial dislocation from free surface³². *In situ* experiments also showed that the surface nucleation of dislocations could operate in a wide size range in FCC nanostructures, from the angstrom scale^{48,49} to the sub-micrometer scale (more than 200 nm)³⁴. Moreover, surface nucleation also acts as the prevalent deformation mode in nanosized metals with other structures. For example, during the [112] loading of BCC W nanowires¹³, $1/2\langle 111 \rangle$ -type mixed dislocations on the (101) slip planes were frequently observed to nucleate simultaneously from multiple surface sites (Figure 2d-e). Most of these dislocations were nucleated as dipoles, which should be the half dislocation loops on the (101) planes. Dislocations in dipoles can expand on their slip planes under further loading (Figure 2f-g), contributing to plastic deformation. However, the nature of those dipoles and the effects of surface structures on dislocation nucleation in BCC metals need to be further studied. Yu *et al.*⁵⁰ also revealed

a surface-mediated twinning process in hexagonal-close packed (HCP) Mg single crystal nanopillars. But the detailed atomic mechanism of twinning remains unclear.

Figure 3. Formation of the dislocation-originated SFT. (a-c) Deformation snapshots of the dislocation structure evolution and the dislocation-originated SFT formation in a $[111]$ -loaded Au nanowire. The yellow triangle in the inset of (c) labeled out the fully-developed SFT. Scale bar in (a-c), 5 nm. (d) MD simulation revealed that the dislocation-originated SFT was formed via a sequential process of partial dislocation interactions and cross-slip. Reprinted with permission from Ref.⁵¹. © 2013 Nature Publishing Group.

Dislocations in the nanosized crystals can escape from the small volume easily due to their proximity to the free surface that imposes large attractive image forces on dislocations. However, interactions between dislocations may also be facilitated by the small volume, given the abundant surface sources^{11,32,35}. Wang *et al.*⁵¹ discovered a novel interaction mechanism of dislocation-originated stacking fault tetrahedra (SFT) in Au nanowires (Figure 3). For an Au nanowire under axial loading, partial dislocations nucleated on the equivalent, inclined $\{111\}$ planes from different surface sites and those partials interacted with each other, forming dislocation junctions. Upon further loading, the sessile junctions evolved into nanosized SFT through cross slip of a partial dislocation on the base plane of the SFT. Such dislocation-originated SFT were frequently observed in Au nanowires with different sizes and orientations, and the formation mechanism is also applicable to other FCC metals and alloys with medium-to-low stacking fault energies (SFE), such as Cu⁵¹. Moreover, the surface-nucleated

dislocations could also accumulate inside the small volume, generating a low angle grain boundary (GB)⁵². Thus, the dislocation interaction and dislocation-originated SFT may play an important role in the plastic deformation of nanocrystals.

4. Size-dependent transition of deformation mechanisms

Dislocation slip and deformation twinning are the competing deformation modes in crystals. In bulk BCC materials and FCC materials with medium-to-high SFEs, the room temperature plasticity is usually controlled by dislocation slip, while twinning only prevails under extreme deformation conditions, such as low temperature and high strain rate⁵³⁻⁵⁵. As the feature size decreases (including grain size and crystal size), the stress in small crystal volumes can become so high that deformation twinning dominates over dislocation slip^{1,14}. The size-dependent competition between dislocation and deformation twinning has been frequently reported.

As the grain size decreases, deformation twinning can become a dominant deformation mode in nanocrystalline FCC metals and alloys with medium-to-high SFEs, such as Al, Ni and Cu^{54,56,57}. Using *in situ* straining, Li *et al.*⁵⁸⁻⁶⁰ revealed that the deformation twinning at crack tips of Al thin films and Ni nanocrystals was reversible, such that the twinned region returned to its original orientation via a detwinning process. The detwinning was possibly driven by the large surface image forces on twin partials, high SFE and low Peierls-Nabarro stresses that resist the motion of partials on twin boundaries (TBs)⁵⁸. A similar size dependence of dislocation-to-twinning transition also occurs in a variety of metals and alloys when the crystal size is reduced. For instance, Seo *et al.*⁶¹, Sedlmayr *et al.*⁶², Roos *et al.*⁶³ and Oh *et al.*⁶⁴ reported the twinning dominated deformation in Au nanowires, nanowhiskers and thin films. Deformation twins formed

via layer-by-layer movement of twin partials that nucleated from the free surface, and the migration of coherent TBs could contribute to the superplastic deformation in Au nanowires⁶¹. Recently, Yue *et al.*⁶⁵ quantitatively studied the size dependence of deformation transition in Cu single crystal nanowires with a wide size range, from 1000 nm to 70 nm. At the relative large scale (> 150 nm), full dislocations controlled the plastic deformation; however, partial dislocations and/or deformation twins became the major deformation carriers below 150 nm.

Figure 4 Twinning-dominated deformation in a W nanowire. The nanowire was compressed along $[110]$ under a strain rate of 10^{-3} s^{-1} . (a-c) Twinning process in a W nanowire at room temperature. Scale bars, 5 nm. (d-e) Fast-Fourier transformed (FFT) patterns showing the structure of the original W nanowire and the deformation twinning, respectively. (f) A zoomed-in image of the deformation twinning. Scale bar, 1 nm. Reprinted with permission from Ref.13¹³. © 2015 Nature Publishing Group.

Only dislocation activities were reported in the deformation of bulk and small BCC metals at room temperature^{45,66-71}. However, a recent *in situ* TEM nanomechanical study showed that twinning became the dominant deformation mode in BCC W nanowires with different orientations under room temperature and low strain rates, as the crystal size was reduced to ~ 20 nm (Figure 4)¹³. Under compression, a twin embryo emitted from the GB-surface intersection, and then expanded laterally to penetrate into the nanowire (Figure 4b). As the load was increased, the twin band thickened through layer-by-layer movement of the twin boundary (Figure 4c). Under cyclic loading, the W

nanowire exhibited a pseudoelastic deformation via reversible twinning-detwinning. For HCP metals, Yu *et al.*³¹ demonstrated a size-dependent deformation transition from deformation twinning to ordinary dislocation plasticity in Ti alloy. Although such transition was attributed to the “stimulated slip” mechanism, the actual deformation mechanism controlling the transition remains unclear and needs to be further studied.

The size-dependent deformation was even observed at the angstrom scale. Lagos *et al.*⁴⁹ found that the gliding directions of preferred fault in Au and Pt nanorods with few atom-layers were also determined by their sizes and shapes. In Au nanowires with the angstrom-scale fine structure of nanotwins, even the defect nucleation mode can be changed with the reduction of twin size³⁵. Moreover, both crystal orientation and side surface could affect the competition between dislocation slip and deformation twinning². The influence of orientation can be analyzed in terms of the Schmid factors of the leading and trailing partials². However, the effect of side surface on deformation remains largely unclear and thus calls for the systematic study through both experiments and simulations.

5. Atomistic deformation mechanisms in nanotwinned metals

Nanoscale twinning is an effective means of achieving the unusual combination of superior mechanical and physical properties, including ultrahigh strength^{35,72}, high ductility⁷³ and fatigue resistance⁷⁴⁻⁷⁶, high electrical conductivity^{73,77} and radiation tolerance^{78,79}. Considerable effort has been devoted to understand the atomistic mechanisms that control the unique mechanical properties in nanotwinned metals.

The dislocation processes at TBs can critically control the hardening and plasticity of nanotwinned materials. TBs can act as the strong barriers to dislocation motion, resulting in strain hardening. Dislocations can transmit through and/or multiply

at TBs, contributing to plasticity⁸⁰⁻⁸⁴. Wang *et al.* revealed that the initial plastic deformation of nanotwinned Cu was mediated by the migration of coherent TBs, which proceeded through the emission of Shockley partial dislocations from the TB-GB intersections⁸⁵. The coherent TBs were also able to act as effective dislocation sources for the continual deformation. And this process was facilitated by the atomic steps on coherent TBs^{85,86}. When transmitting through a coherent TB, the extended dislocation will shrink firstly to form a full dislocation near the TB, which then re-dissociates into partials after the transmission and leaves behind a detwinning partial dislocation at the TB⁸⁰. Recently, Li *et al.*^{37,87} found that the twinning dislocation was able to multiply at the coherent TB via two dissociation processes. In the first step, a full dislocation trapped by the coherent TB dissociated into a Frank partial disconnection and a twinning dislocation; after the first twinning partial moved away, the Frank partial at TB could further dissociate into a full dislocation and a new twinning dislocation, accompanied by a translational shift of the Frank defect^{37,87}. Both dissociations were driven by the applied shear stress parallel to the TB, and the motion of twinning dislocations on a twin plane could result in TB migration^{37,87}. It was also revealed that the dynamic crack propagation at a coherent TB involved the alternating processes of crack blunting, crack deflection, twinning/detwinning and slip transmission across TBs, which contributed to the improved fracture resistance^{83,84}.

The $\Sigma 3$ {112} incoherent TB is common in nanotwinned metals. Interactions between dislocations and incoherent TBs can also induce TB migration, twinning or detwinning. The migration of incoherent TBs could proceed through different mechanisms. For example, Wang *et al.*^{81,82} reported that in a nanotwinned Cu film, the

migration of an incoherent TB and the subsequent detwinning was mediated by the glide of multiple twinning dislocations that form the $\Sigma 3$ $\{112\}$ incoherent TB; while Liu *et al.*⁸⁸ discovered a screw-rotation mechanism of the incoherent TB in nanocrystalline Au, in which the migration proceeded in a manner of consecutive and collective screw-rotations of triple-partials along the $[111]$ screw-axis of the TB. In addition, an incoherent TB can also migrate via the interaction with a gliding dislocation. For example, a gliding $1/3[111]$ partial dislocation on an incoherent TB could exchange its position with TB dislocations in sequence, leading to migration of the incoherent TB toward its normal direction⁸⁹. The migration of incoherent TBs can result in twinning or detwinning^{88,90}.

Figure 5 Twin-size dependent mechanical property and deformation mechanism in nanotwinned Au nanowires. (a) Representative stress-strain curves of Au nanowires with no twin, low density twins (LDTs), bimodal twins and ultrahigh density twins (UDTs). The inset shows a zoomed-in image of the angstrom-scale twins and $\{111\}$ surface microfaceting in the nanotwinned Au nanowire. (b) Atomistic lattice strain measurements showing a Hall-Petch type behavior in the elastic strain limit of nanotwinned $[111]$ -Au nanowires. (c) Heterogeneous nucleation of dislocation from free surface in Au nanowire with LDTs ($\lambda = 12$ nm). (d) Homogeneous dislocation nucleation in Au nanowires with bimodal twins. Reprinted with permission from Ref.35³⁵ and Ref.91⁹¹. © 2013 Nature Publishing Group. © 2015 American Chemical Society.

The twin size (λ) can strongly influence the mechanical properties of nanotwinned metals. In nanotwinned Cu, a maximum strength was achieved at the twin size of ~ 15 nm and further reduction of λ resulted in a softening⁹². Recently, Lu *et al.*⁹³

revealed that the twin-size dependent mechanical properties of nanotwinned Cu originated from the transition of dislocation nucleation sources. When λ was less than ~ 18 nm, the dominant mode of dislocation nucleation in nanotwinned Cu gradually transited from the atomic-scale steps on the TBs to the junctions between TBs and GBs. The competition in dislocation sources was governed by the local stress concentration at those nucleation sites, which varied significantly with the twin size. Such transition in dislocation sources dominated the change of macroscopic mechanical properties in nanotwinned Cu. A similar twin-size dependence of plastic deformation was also reported in nanotwinned metallic nanowires, but via different controlling processes. Jang *et al.*^{15,94} used the electroplating template to synthesize the vertically-aligned nanopillar arrays of nanotwinned Cu, and further investigated the effects of diameter, λ and TB orientation on the mechanical responses of individual pillars. Nanopillars with orthogonally oriented TBs showed a brittle-to-ductile transition when the λ was reduced below $\sim 3\text{--}4$ nm. In this case, the deformation was controlled by strain localization at the TB-dislocation interactions. In contrast, shear offsets and significant detwinning dominated the deformation of nanopillars with slanted TBs¹⁵. Recently, Wang *et al.*^{35,91} reported the twin-size dependent deformation in Au nanowires with angstrom-scale twins (Figure 5). When λ was reduced down to the angstrom scale ($\lambda < 2.8$ nm), Au nanowires exhibited a remarkable ductile-to-brittle transition as well as the near-ideal strength (Figure 5a), while the elastic strain limit showed a strong Hall-Petch type strengthening (Figure 5b). That is, when $\lambda > 2.8$ nm, the elastic strain limits of nanotwinned Au nanowires can be linearly related to $\lambda^{-1/2}$; the near ideal elastic strain limit (up to 5.3%) was achieved as λ decreased below 2.8 nm (Figure 5b). The Hall-Petch type

strengthening on the elastic strain limit originated from the image effect induced by the repulsive force of TBs on gliding dislocations. The deformation in Au nanowires without twins or with large twins was controlled by the heterogeneous nucleation of dislocations from free surface that required a relative low stress, leading to an earlier yielding but good ductility (Figure 5c). However, the angstrom-scale twins suppressed the heterogeneous nucleation of dislocations from free surface, such that the homogeneous nucleation of dislocations inside the nanowires dominated the onset of yielding, resulting in an ultrahigh strength (Figure 5d). The homogeneous nucleation caused an avalanche of new dislocations, leading to shear localization, necking and thus brittle fracture. Such a transition of heterogeneous-to-homogeneous dislocation nucleation is responsible to the ductile-to-brittle transition in nanotwinned Au nanowires. The twin size effects on dislocation nucleation were also observed during bending of nanotwinned Ni nanowires⁹⁵. With the reduction of λ , the dominated deformation mode in bent Ni nanowires gradually transited from the nucleation of full dislocations ($\lambda > 12$ nm) to the nucleation and glide of full and partial dislocations on multiple slip systems ($9 \text{ nm} < \lambda < 12 \text{ nm}$), to the nucleation of partials that subsequently glide on the slip planes intersecting TBs ($6 \text{ nm} < \lambda < 9 \text{ nm}$), to the partial nucleation and gliding parallel to TBs ($1 \text{ nm} < \lambda < 6 \text{ nm}$), and finally to the TB migration and detwinning ($\lambda < 1 \text{ nm}$)⁹⁵. Those twin-size dependent deformation and mechanical properties are different from the crystal size effect described previously.

Additionally, *in situ* nanomechanical testing also revealed the Bauschinger effect and recoverable plasticity in penta-twinned Ag nanowires⁹⁶⁻⁹⁸, strain hardening in Al films with incoherent TBs^{99,100}, TB migration and detwinning in nanotwinned films and

nanowires¹⁰⁰⁻¹⁰², and irradiation tolerance of nanotwinned metals¹⁰³⁻¹⁰⁵. However, a complete atomistic understanding of those novel phenomena, particularly regarding the deformation mechanism in defective twin boundaries¹⁰⁶, is still lacking and thus requires further study in the future.

6. Phase transformation, liquid-like behavior and pseudoelasticity

The ultrahigh stress and large surface image force in nanostructured materials can give rise to unexpected deformation phenomena, while the high surface energy of nanomaterials facilitate the atom diffusion and structural reconstruction. Both *in situ* experiments and MD simulations have revealed unique deformation phenomena in nanostructured materials, such as phase transformation^{32,107,108}, liquid-like behavior^{33,109}, pseudoelasticity^{13,33,52,110} and crystallographic reorientation¹¹¹.

In situ HRTEM straining showed that both the surface stress and mechanical loading could induce the phase transformation in metallic nanostructures. Zheng *et al.*³² reported a surface-mediated FCC-to-body-centered tetragonal (BCT) transition after the fracture of an Au nanowire (Figure 6). At the moment of fracture, significant structure relaxation occurred in the bottom half of the Au nanowire, resulting in a contraction along the [001] axial direction (Figure 6a-b). The structure relaxation was accompanied by the formation of a new BCT phase (Figure 6c-f). Such FCC-to-BCT transition in Au nanowire was driven by the surface-induced compressive stress that exceeded the compressive stress required to transform the FCC-Au to its metastable state of BCT-Au with higher energy³². The FCC-to-BCT phase transition was also observed during *in situ* straining of an Au nano-junction, but proceeded through a progressive slip process¹¹². Other factors, such as crystallographic orientation, size and beam irradiation, may

influence the phase transformation in Au nanostructures^{32,113}. For instance, Zheng *et al.*³² observed that the FCC-to-BCT phase transformation only occurred in $\langle 001 \rangle$ -loaded Au nanowires. However, in another study, a FCC-to-HCP transition happened when a $\langle 110 \rangle$ Au nanowire was thinned below 2 nm under electron beam irradiation¹¹³. Moreover, the deformation of BCC metals could also proceed via phase transformation. Wang *et al.*¹⁰⁸ showed a sequential phase transformation process at a crack tip of Mo thin film under mechanical loading. At the crack tip, the $\langle 001 \rangle$ -oriented BCC Mo initially transformed to a $\langle 001 \rangle$ -oriented FCC phase, and then reverted to a $\langle 111 \rangle$ -oriented BCC structure. Such sequential phase transformation could contribute to large lattice rotation for accommodating the plastic deformation of BCC metals¹⁰⁸.

Figure 6 Surface-mediated phase transformation in a fractured Au nanowire. (a-b) Structure relaxation resulted in the contraction of the bottom half of Au nanowire after its fracture. Scale bars, 3 nm. (c-d) Zoomed-in HRTEM images showing the atomic structure of the selected areas in (a) and (b), respectively. (e-f) Simulated HRTEM image of FCC-Au with $a = 4.078 \text{ \AA}$ in $[110]$ zone and BCT-Au with $a = b = 3.34 \text{ \AA}$ and $c = 2.86 \text{ \AA}$ in $[100]$ zone, respectively. (g) FCC-BCT martensitic transition via the Bain path,

caused by the lattice distortion along the [001] direction of FCC crystal. The FCC and BCT unit cells were labeled out by black and blue lines, respectively. Reprinted with permission from Ref.³². © 2015 Nature Publishing Group.

The high mobility of atoms in nanomaterials could promote the diffusion-controlled deformation. Au nanocrystals, for instance, showed a liquid-like behavior during the *in situ* friction at 166 °C¹¹⁴. Recently, Sun *et al.*³³ reported that the crystalline Ag nanoparticles can deform like a liquid droplet at room temperature, without observable dislocation activity. Such liquid-like deformation of Ag nanoparticles was attributed to the fast diffusion of surface atoms, driven by either an external force or capillary-energy minimization. However, whether the liquid-like deformation in metallic nanostructures involves a temperature increase remains debated. Yue *et al.*¹⁰⁹ showed a crystalline-liquid-rubber-like behavior during fracture of Cu nanowires, with a retractable strain of ~35% after fracture. But this crystalline-liquid-rubber-like behavior was attributed to an instant release of the ultrahigh elastic energy that was stored in the nanowires and the resulting temperature increase at the fracture tip that enhanced the atomic diffusion¹⁰⁹. Additionally, the rapid surface diffusion can be also beneficial to plastic flow in nanostructured glasses^{115,116}, and for example give rise to superelongation in the brittle glass¹¹⁵.

Both the phase transformation and diffusion-mediated liquid-like deformation can result in the pseudoelastic deformation in metallic nanostructures^{3,33}. The reversible twinning-detwinning during cyclic loading was also observed to underlie the pseudoelastic deformation of metallic nanostructures, such as W and Ni^{13,59}. Recently, a dislocation-mediated pseudoelastic deformation was observed during the *in situ* bending of an Au nanobridge⁵². Instead of annihilating to the free surface³², the surface-nucleated

dislocations piled up inside the small crystal under bending, creating a low angle GB (LAGB)⁵². However, removal of the external loading resulted in dissociation of the LAGB, and the crystal recovered its original orientation after the complete annihilation of GB dislocations to free surface⁵². Such dislocation-mediated pseudoelasticity in Au nanobridge originated from the large surface stress and the back stress induced by the structural relaxation⁵².

Experimental and theoretical studies also showed other surface and deformation mediated phenomena in nanostructured materials, such as shape memory effect¹¹⁰, reorientation¹¹¹, martensitic transformation¹¹⁷ and deformation-induced amorphization¹¹⁸. However, further *in situ* experimental study is needed to understand the atomistic mechanisms controlling those unconventional deformation phenomena.

7. Atomistic deformation mechanisms in nanocrystalline metals

The mechanical properties and deformation of nanocrystalline materials are usually dominated by the GB-mediated processes^{119,120}, including GB sliding/migration, grain rotation, dislocation source annihilation inside nanograins, and dislocation nucleation from GBs. *In situ* nanomechanical testing have revealed the GB-mediated plasticity via grain agglomeration in nanocrystalline Ni with an average grain size of ~ 10 nm²⁷. Below a critical grain size, grain rotation becomes a dominant deformation mode in nanocrystalline materials. In nanocrystalline Pt films, for instance, the coordinated rotation of multiple grains controlled the deformation when the grain size was less than 6 nm¹²¹. However, grain rotation proceeded via the dislocation climb at GBs, rather than the generally-believed GB sliding or diffusional creep¹²¹. *In situ* nanomechanical testing

also revealed the GB-mediated crack propagation in nanocrystalline Au¹²², involving the nucleation and motion of atomic steps at the crack tip.

It is believed that nanocrystalline materials have a negligible dislocation storage ability, since the dislocations can annihilate at GBs easily^{119,120}. However, a recent *in situ* TEM study showed that dislocations in nanocrystalline Pt film were very active and able to accumulate inside nanograins (~ 10 nm)^{123,124}. When the grain size was larger than 10 nm, full dislocations interacted with each other inside nanograins, forming stable Lomer locks, while partial dislocations with SFs were prevalent in the smaller grains¹²³. As dislocations accumulated in the nanograins of Pt film, a high dislocation density, up to $6.4 \times 10^{16} \text{ m}^{-2}$, was achieved¹²⁴, in contrast to the widely-accepted notion of negligible dislocation storage in nanocrystalline materials^{119,120}. Moreover, although GBs acted as the preferred sites of dislocation absorption in nanocrystalline materials, the reduction of dislocation density in nanocrystalline Pt film mainly occurred via the formation and annihilation of dislocation dipoles inside nanograins¹²⁴. Those unexpected dynamic dislocation processes could contribute to the high rate sensitivity of nanocrystalline materials^{125,126}. Given the high defect density and the confined volume, dislocations may self-annihilate inside nanograins and thus result in a structural relaxation, contributing to the rate-dependent deformation. This notion was confirmed by Colla *et al.*¹²⁷ via a time-resolved creep test in nanograined Pd films. It was shown that the time-dependent structural relaxation of Pd films with the grain size of about 30 nm was controlled by the gradual annihilation of dislocations, instead of the GB-controlled process. Those discoveries revealed the important roles of dislocation activities in the plastic deformation of nanocrystalline materials.

8. Atomistic bending and fatigue mechanisms

Bending and fatigue are two important damage modes of materials. The nanoscale bending and fatigue mechanisms are of both scientific and technological interests for the miniaturization of MEMS devices. The bending testings in either AFM or SEM have revealed the ultrahigh strength^{21,128}, size and orientation dependence of mechanical properties^{21,129}, deformation and failure^{130,131} in metallic, ceramic and semiconductor nanostructures. However, those studies cannot resolve the atomic-level bending deformation and failure mechanisms yet.

Figure 7 Reversible lattice deformation pathway beyond the elastic strain limit. (a) Atomically-resolved lattice of a Ni nanowire under a bending strain of $\sim 1.9\%$. (b) HRTEM image showing that the lattice shear angle increases continuously in the bent region, from 71° to 109° . Insets are the simulated HRTEM images at the local area. (c) Deformation snapshot after release of the bending strain, without observable lattice distortion, suggesting that the large lattice strain of 34.6% was completely released. (d) Atomic deformation configurations in (b), showing the ultrahigh lattice shear, increasing

from 0 to 34.6% continually. (e-g) The change of 3D lattice structures during the bending shear and recover process, along with their side views. Scale bars, 1 nm. Reprinted with permission from Ref.¹³². © 2015 Nature Publishing Group.

The *in situ* TEM method has been recently employed to study the bending of nanostructured materials¹³³⁻¹³⁵. Han's group developed a novel technique of bending using a cracked colloidal thin film for characterizing the atomic-scale bending deformation in semiconductor and metallic nanowires^{95,132,136-138}. Their analysis of atomic-level strains indicated that as the bending strain increased, the neutral axis in the Si nanowires gradually shifted from the compressive to the tensile side¹³⁷. Accompanied with the bending are the frequent and diverse dislocation events, including nucleation, motion, interaction and annihilation, resulting in the inelastic instability and incipient plasticity in brittle nanowires. Further bending caused the localized lattice distortion and structural amorphization in the Si nanowire near the cores of Lomer dislocations¹³⁶⁻¹³⁸. The bending deformation of metallic nanowires (*e.g.*, Ni), however, is completely different from those of brittle semiconductor nanowires^{95,132}. For example, large reversible deformation and shear strain (up to 34.6%) can be achieved in the Ni nanowires under bending, which is four times higher than the theoretical elastic strain limit of Ni. Such reversible bending strain in Ni nanowires was caused by a continuous and gradual lattice deformation via sequential phase transformations (Figure 7a-c). That is, the initial FCC lattice gradually transited to a BCT structure via a orthogonal path under bending, and then reoriented into a new FCC lattice (Figure 7d-e)¹³². It is worth noting that the microstructure of nanowires, such as nanotwins, could further affect the bending deformation of Ni nanowires, inducing a twin-size dependence of the bending mechanism⁹⁵.

In addition to the aforementioned studies of semiconductor and metallic nanowires, the bending-induced fatigue of Al-based metallic glass was reported by Wang *et al.*¹³⁹ Under cyclic straining, nanoscale surface roughening occurred progressively in the highly deformed region of the initial notch in an Al-based metallic glass beam, causing the crack nucleation and nanocrystallization at the crack tip. The growth of nanocrystals at a crack tip impeded the subsequent crack growth by crack bridging¹³⁹. Moreover, Lee *et al.* investigated the cyclic deformation of the [110]-oriented Au nanowires under uniaxial loading¹⁴⁰. Twinning and consecutive detwinning occurred in the tension-compression cycles, and thereby dominated the reversible plastic deformation and cyclic damage in Au nanowires¹⁴⁰. These studies provide new insights into the deformation and fatigue mechanisms under bending, beyond the usual deformation modes of axial tension and compression in nanomaterials.

9. Summary and Outlook

In situ TEM nanomechanical testing has proved itself as a powerful approach to study the dynamic deformation behavior of nanostructured materials at multiple length scales. The recent advance in TEM characterization techniques, such as the aberration-corrected TEM¹⁴¹ and ultrafast camera for electron detection and data recording¹⁴², are expected to further push the limit of the *in situ* experimental mechanics down to the sub-angstrom and millisecond scales in the near future, thereby providing new opportunities of studying the ultrafast defect dynamics. Double-tilt straining holder needs to be developed for enabling the flexible atomic-scale imaging¹⁴³. Moreover, the development of MEMS device and environmental TEM enables us to conduct the nanomechanical testing at controlled temperatures^{144,145} and environmental conditions^{146,147}. One

challenge might be the sample stability and drift under those conditions, which critically limit the resolution. In addition, special care is required to avoid the electron beam induced artifacts during the *in situ* nanomechanical testing and data analysis¹⁴⁸.

We have identified several areas that we believe present particularly pressing research needs and opportunities in the future, in order to establish a complete structure-property-deformation map of nanostructured materials:

1. The crystal structure can affect the defect nucleation and evolution⁹, while the surface facets and side surfaces strongly influence the defect nucleation and deformation in nanomaterials with large surface areas^{2,46,149}. An understanding of the crystal and surface structures on the defect dynamics would benefit the controlled synthesis of advanced nanomaterials. Moreover, how the interfaces in multilayer and nanolaminate materials affect the defect nucleation and deformation remains largely unexplored by *in situ* experiments. In addition, effects of the local solute concentrations and distributions on the dislocation motion in engineering alloys have not been directly studied by *in situ* experiments at the atomic scale¹⁵⁰. Combining the atomic-level *in situ* nanomechanical testing and computational modeling provides a promising means to address these challenges.
2. For the nanotwinned materials, the current study has focused on the deformation of parallel TBs. However, twin-twin junctions and hierarchical nanotwins frequently formed during the deformation of engineering alloys. Revealing the formation and deformation process of these highly-ordered twin structures will be helpful to engineer 3D nanotwins for achieving the optimal strength and ductility. In addition,

understanding both the deformation of defective TBs and the sliding of TBs are important for development of the nanotwinned materials.

3. In nanocrystalline materials, the GB-mediated deformation usually leads to grain coarsening and deformation softening. Visualizing the time-resolved atomic-scale GB process is essential for finding means of stabilizing nanograins, and broadly for engineering the ultrafine-grained and nanocrystalline materials with both mechanical and thermal stabilities.
4. The environmental TEM provides a new opportunity of studying the time-dependent dynamic processes of creep, stress corrosion and hydrogen embrittlement in engineering alloys under controlled environmental conditions. The associated TEM results can be also used to validate the modeling and simulation of material degradation in the practical applications.
5. The properties of functional materials (*e.g.*, semiconductor and graphene) are significantly influenced by the defects and applied strains. Revealing the mechanical responses of those functional materials is thus critical for their applications. *In situ* nanomechanical testing has been recently employed to study the mechanical deformation in functional materials, such as graphene^{142,171}, GaN and GaAs nanowires^{38,151}. However, the systematic nanomechanical studies are needed to establish a complete structure-property relationship in a wide range of functional materials, especially at the atomic scale.
6. The recent development of *in situ* testing under electronic and electrochemical conditions^{39,152,153} opens a new avenue to study the atomic-scale structural changes under the multiphysical environment and subjected to the electro-mechanical and

electro-chemo-mechanical loads. The *in situ* nanomechanics research in this direction will help develop strategies for the design and application of energy-storage materials and MEMS devices.

In summary, the *in situ* atomic-scale nanomechanical testing is an emerging research direction in experimental mechanics, and will provide novel insights into the structure-property-mechanism relationships of nanostructured materials under different mechanical and multiphysical loading conditions. Through *in situ* nanomechanical experiments, we can achieve an unprecedented ability of resolving the atomic-scale dynamic processes in advanced engineering and functional materials, which will ultimately revolutionize the design of novel materials and devices from the smallest bottom.

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