Defect engineering, a path to make ultra-high strength low-dimensional nanostructures

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A current understanding is that materials with perfect structures have better mechanical properties. Thus, lowering the defect concentration, particularly by reducing the size of synthesized materials such as nanowires (NWs), is one of the key goals in the fabrication of new materials. In contrast, here we demonstrate the possibility of enhancing the mechanical properties of the low-dimensional nanostructures by engineering defects using the classical molecular dynamics technique. Our results show that NWs with high-density of I\textsubscript{1} stacking faults (I\textsubscript{1}-SFs) have higher Young’s Module (up to 14% in compression) and critical stress (about 37% under compression) in comparison to the perfect structure over a wide range of temperatures. This enhancement is in agreement with the in-situ experimental measurements of highly defective NWs and is explained by the interplay between surface stresses and the stress field of immobile SFs. The overlap of SF-induced stresses in regions confined by SFs partially relaxes with increasing temperature, while it remains the main reason for this non-trivial strengthening. Furthermore, a unique stress relaxation mechanism, twin boundary formation, is revealed for highly defective NWs. The twin boundary formation postpones the phase transition and increases the resilience of the nanostructure over a wide range of temperatures, which results in a stress plateau in a highly defective NW and an increase in ductility. Defect engineering is demonstrated as a new route for synthesizing advanced materials with superior mechanical properties, and increasing their stiffness, strength, and ductility for applications under extreme environments.

1. Introduction

One-dimensional nanomaterials, nanotubes (NT), nanowires (NWs), nanorods (NRs), and nanobelts (NBs), are promising candidates for sensors [1], lasers [2], optoelectronics [3], and photocatalysts [4]. The response of these one-dimensional (1D) materials highly depends on the size, defect concentration, and structure. Therefore, to achieve the desired characteristics (e.g., electrical, mechanical, and optical), the growth condition should be controlled. There is a long-standing notion among researchers that the perfect structure is the ideal form of material in terms of mechanical properties, and intrinsic defects (e.g., point and planar defects) degrade the mechanical properties. So, defects have been treated as unwanted constituents that should be removed from the material or have their concentration reduced, e.g., by precise controlling of the growth process [5,6]. Here, our main goal is to understand the correlation between defect structure and properties in low-dimensional materials and seek a way to enhance mechanical performance of this class of materials by engineering inherent structural defects. This will open up a new avenue for design materials with tunable properties and subsequently expand the design space.

The tuning of material properties by modifying defect concentration has recently attracted a great deal of attention in the research community. This topic is of great importance when one deals with nanostructured materials, because their response highly depends on the defect size, type, and concentration, e.g., doping the nanostructures with specific elements can change their electrical properties [7]. Furthermore, experimental [8] and numerical studies [9] show that the radiation tolerance of nanocrystalline SiC (nc-SiC) with a high density of SFs can be enhanced by an order of magnitude. A few experimental studies show that systematically introducing nano-twin boundaries in Cu [10] or stacking faults (SFs) [11,12] in GaAs NWs enhances the mechanical properties that can be achieved by precise control over the synthesizing process [13]. Also, introducing twins in Ag [14] and Ni [15] NW alters the deformation mechanism - i.e. plasticity and...
dislocation nucleation. Additionally, MD simulations confirmed this strengthening mechanism in SiC [16] and ZnO NWs [17] at T = 0 K and relatively low density of the SFs. These studies predicted the strengthening mechanism, although the stress relaxation mechanism is still unchanged; the stress drops due to the phase transition or fracture. This careful engineering of internal defects creates barriers for dislocation motion or phase transition and subsequently alters the physical properties of nanostructures. Despite the fact that manipulating internal defects, e.g., adding precipitates or grain refinement to enhance the yield strength, is a common method at the macroscale level, it has not been well-studied at the nanoscale level. It is worth mentioning that the strengthening methods in macroscale have their own setbacks, like a reduction in ductility [18] that can be overcome in nanoscale. However, on the other side of the spectrum, there is a long-standing notion that these defects are the root cause of structural weakening [19–24]; consequently, there is not a consensus on the exact effects of the defects on mechanical properties. Therefore, understanding the underlying physics opens a new avenue through which to predict, design, and fabricate a new class of one-dimensional materials with superior properties. Here, we showed that this enhancement in mechanical properties can be achieved over a wide temperature range, T = 100–500 K. Also, a new stress relaxation mechanism for ZnO NWs, twin formation, was predicted for high density of SFs, which is unprecedented.

2. Computational model

In order to study the potential strengthening mechanism in defect-engineered low-dimensional materials, ZnO NWs are chosen as the model material due to their technological importance [25–28]. The stable structure for ZnO NWs is Wurtzite (WZ) that consists of stacking ABABABAB; each letter corresponds to a layer including zinc and oxygen atom. The I1-SF is the most common planar defect in ZnO NWs [29], which changes the stacking sequence to ABAB|CBCB so that the fault is placed between layer B and C. This planar defect was frequently observed in synthesized NWs due to their low formation energy [30]. The I1-SF burger vector R = (1/3)[0110] + (1/2)[0001] [29] can be generated by removing a layer from the perfect crystal and moving the other portion of NW by R. The schematic for faulted NW is shown in Fig. 1a.

Initially, the NW was relaxed for 500 ps at various simulation temperatures, T = 100–500 K, under NVE ensemble to equilibrate the energy. The relaxation time was chosen via an iterative process, ensuring that the stress fields of SFs are relaxed. A maximum temperature of 500 K is chosen that is smaller than T_m/3 = 750 K to avoid the emergence of time-dependent behaviors such as creep. Then, the NPT ensemble with a Nose–Hoover thermostat was used for another 500 ps to find the relaxed configuration. In the next stage, a constant strain rate of ± 0.1 ps, to avoid strain-rate dependent responses, was applied along the c-axis, [0 0 0 1], (Fig. 1a) to model the mechanical response of NW under tension/compression. The time step for all simulation cases was 1 fs. All of the simulated NWs have a diameter of 10 nm and are 40 nm in length. The Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code [31] was employed for MD simulations. Various defect density was introduced in NW; the number of stacking faults varies between 2 and 26 that are separated with equal distances. In the bulk structure, SF is constrained between two partial dislocations and can glide over these partial dislocations [32], but due to the high surface-to-volume ratio of NWs, these planar defects are pinned at the external surfaces and are immobile. The radial distribution function test was performed on the WZ NW to find the lattice parameters; see Fig. 1b. The calculated c/a ratio is 1.55, which is close to the previous DFT calculations (c/a = 1.6) [33], MD simulations (c/a = 1.57) [33], and experimental measurements (c/a = 1.606) [34]. The difference between the obtained ratios is due to the size effect.

To ensure the validity of our simulations, the formation energy of I1-SF and the bulk Young’s of WZ structure was calculated. At room temperature, Young’s Modulus is 146 GPa, which is in agreement with experimental studies, ≈ 140 GPa [35]. Also, the formation energy is 14.1 meV/unit-cell area, which is close to the density functional theory calculations 15 meV/ (unit-cell area) [30]; the detailed calculation can be found in Refs. [17,36].

3. Results and discussion

The stress-strain curve for the perfect 1D-nanostructures follows a sawtooth pattern. The stress increases with increasing strain, and elastic energy gradually accumulates in the material until it reaches a critical value, i.e. critical stress [36–39]. At this point, the structure releases the elastic energy via a stress relaxation mechanism, e.g., dislocation nucleation/phase transition, which can be designated as a critical strain. The simulated stress-strain curves for a perfect and defective NWs with 2, 13, and 26 SFs are plotted in Figs. 2–5 for T = 300 K. Fig. 2 shows the response of a perfect NW under tensile/compression loading and the associated phase transition as a common stress relaxation mechanism in perfect ZnO NWs [33,36,39,40]. In compression, nucleation of hexagonal (HX) polymorph leads to a drop in stress (point PFF), and nucleation of a body center tetragonal polymorph (BCT) (point PFF) releases the stress in tension. The coordination analysis was performed to visualize the nucleation and propagation of new polymorphs (HX and
BCT) during loading; see Fig. 2b–c. In a perfect NW, the nucleus of the new phase appears at the free surface due to the atoms at the surface having larger energy and being more prone to phase transition. In compression, the new HX nucleus appear in two regions on the free surfaces; the HX phase is shown by the red in Fig. 2a, and will propagate with increasing strain (PC3). A similar phenomenon is observed for tension; nucleation of BCT at the free surfaces (Fig. 2c, point PT2), however, in this case, the NW is completely transformed to BCT polymorph at the large strains (Fig. 2c, point PT3).

In the next step, different densities of SFs are introduced in the NW, and a tensile/compression test was performed to investigate the effect of SFs on deformation, stress relaxation, and phase transition. The stress-strain curves for three representative NWs with different SF densities are plotted in Figs. 3–5. It is worth noting that the PT (WZ → HX and WZ → BCT) was observed for various SFs density; however, the nucleation sites and kinetics of PT were affected by SFs density (see Figs. 3–5). Fig. 3 shows the compressive and tensile stress-strain curve for a NW with two SFs ($\rho_{SF} = SSF/\mu m$). In the defected NW, the HX phase nucleates between the SFs; three HX regions are observed at SF1 in Fig. 3b. The shift in nucleation sites can be explained by forming highly deformed zones at the intersection of SF and free surface (dashed box in Fig. 3b, point SF1, point P2). In tensile loading, the nucleation is less homogeneous, Fig. 3c, and it starts from one side (point SF2) and gradually propagates along the surface (point SF3). Any further increase in the load leads to propagation of the new phase (BCT) toward the center of NW till the phase transformation (point SF3) completes. By increasing the density of SFs, more nucleation sites are observed between SFs in compressive loading (see Fig. 4, point SF3). The increase in the number of nucleation sites is associated with local SF-induced stress distribution. However, SFs serve as barriers...
to growth and propagation of the new phase. Therefore, one should expect that the required energy for nucleation should be lower than that of perfect structure due to the inhomogeneity in stress distribution along the NW, while the necessary energy for complete phase transition is expected to be higher than the perfect counterpart. The nucleation energy for various temperatures and SF density under compression are summarized in Table 1. The initial reduction in nucleation energy with respect to the perfect NW and its continuous growth by increasing number of SFs verifies the hypothesis mentioned above.

Increasing the SF density to $\rho_{SF} = 625 SF/\mu m$ ($\#SFs = 26$) results in a different mechanical response and unique stress relaxation and phase transition mechanism; see Fig. 5. The SF-induced stress causes phase transition (appearance of BCT phase) at the intersection of SF and free surface in the absence of external loads (dashed box in Fig. 5b, point SF$^{T3,C1}$). A similar WZ to BCT reconstruction has been observed experimentally for nano-islands at surfaces, [41] which proves the feasibility of this transition. A decrease in SF spacing results in an increase in local SF-induced stress due to overlapping stress fields of neighboring SFs, which subsequently facilitates the local transforming of WZ to BCT at the SF/free surface intersection. The stable polymorph under tensile
loading is BCT; therefore one can predict that the appearance of BCT polymorph can lead to an increase in nucleation energy of HX polymorph under compression; note that HX polymorph is stable under compressive loading. The correctness of this postulation can be verified by comparing the nucleation energy of highly defective NW, SF = 26, with its perfect counterpart (see Table 1). Also, in this case, the NW fractures at the SF without exhibiting the phase transition; NWs with low SF density are transformed completely to BCT polymorph under tension (see Fig. 2c, Fig. 3c, Fig. 4c). Therefore, the density of SF can change deformation and failure mode of NWs.

Furthermore, we found a plateau in the compressive stress-strain curve (between SF$^{C1,T1}$ – SF$^{C2}$), indicating significant enhancement in the load-carrying capacity of defective NWs. The underlying physics can be described by arresting the phase transition at SFs and subsequently increasing the required load for nucleation and growth of the high-pressure polymorph within the initial phase. This increase in critical phase transformation load activates a secondary stress relaxation mechanism, i.e. twin boundary formation (Fig. 5b, point SF$^{C4}$). Here, we observed the formation of $\{2112\}$ twin, which is one of the possible ZnO twin planes [42]. Formation of the twin boundary lowers the stress, resulting in the reverse phase transition, i.e., HX to WZ. This new mechanism paves the way to making ultra-high strength, low-dimensional nanostructures via engineering defects.

The total longitudinal strain distribution, $\varepsilon_z$, for different strains in a NW with high density of defects ($\rho_{SF} = 625 SF/\mu m$) is shown in Fig. 6. The strain sign will change (tensile to compressive) at the twin boundary. Also, Fig. 6b depicts the formation of the twin and its structure in more detail, where an initial slice was selected and frozen at equilibrium stage in order to study the deformation. This slice is highlighted in red, and its deformation at the instant of twin formation is illustrated in Fig. 6b.

The stress-strain curve for the highly defective NW
under compressive loading and different temperature is shown in Fig. 7. A stress plateau was identified for a wide range of temperatures, \(T = 100\text{–}500\) K (point a to b in Fig. 7). With increasing temperature, the critical stress is almost constant (the maximum variation in critical stress is less than 4% despite the fact that the temperature varies from 100 to 500 K), whereas the critical strain (i.e., the strain associated with large drop in stress), increases up to \(\varepsilon_c = 0.082\). This behavior is related to the effect of temperature on bond strength (i.e., bond softening). It can be seen that this unique mechanical response makes the highly defective ZnO NWs potential candidate materials for applications at elevated temperatures.

In order to study the effect of SFs on mechanical properties, Young’s Modulus and critical stress of NWs with various defect densities, \(\rho_{SF} = 625 \text{SF}/\mu m\), was examined (Fig. 5). NW with the SF density of 625 SF/\(\mu m\) (#SF = 26). (a) Stress-strain curve. The HX phase appears at multiple sites between SFs under compression (b) and tension (c), and the brittle fracture is observed from the SF location. The coordination number analysis was performed to detect the new phases; the coordination number of HX and BCT is five (red), and WZ has a coordination number of four (green). The snapshots of the crystal structure associated with the vital points, e.g., critical stress, on the stress-strain graph are depicted to illustrate the deformation and phase transition. Superscript “T” represents the stress-strain state on tensile curve and superscript “C” denotes the compression. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

### Table 1

The HX nucleation energy (ev) for different SF density and temperature under compressive loading.

<table>
<thead>
<tr>
<th>#SF</th>
<th>100 K</th>
<th>200 K</th>
<th>300 K</th>
<th>400 K</th>
<th>500 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfect</td>
<td>0.261</td>
<td>0.244</td>
<td>0.239</td>
<td>0.224</td>
<td>0.207</td>
</tr>
<tr>
<td>2</td>
<td>0.185</td>
<td>0.1683</td>
<td>0.163</td>
<td>0.159</td>
<td>0.150</td>
</tr>
<tr>
<td>3</td>
<td>0.181</td>
<td>0.179</td>
<td>0.153</td>
<td>0.158</td>
<td>0.13</td>
</tr>
<tr>
<td>4</td>
<td>0.228</td>
<td>0.217</td>
<td>0.207</td>
<td>0.192</td>
<td>0.186</td>
</tr>
<tr>
<td>6</td>
<td>0.237</td>
<td>0.222</td>
<td>0.211</td>
<td>0.202</td>
<td>0.183</td>
</tr>
<tr>
<td>13</td>
<td>0.242</td>
<td>0.223</td>
<td>0.207</td>
<td>0.207</td>
<td>0.203</td>
</tr>
<tr>
<td>26</td>
<td>0.326</td>
<td>0.293</td>
<td>0.287</td>
<td>0.283</td>
<td>0.285</td>
</tr>
</tbody>
</table>
Temperature, and loading type (compression/tension) were calculated and are shown in Figs. 8 and 9. Fig. 8 shows an increase in Young’s Modulus in tension/compression with increasing density of SFs in all simulated temperatures in comparison to the perfect counterpart. An increase in temperature results in relaxation of SF-induced stress and consequently weakens the strengthening effect; however, a high density of SF (#SF = 13, 26) can still strengthen the material, even at high temperatures. The highly defective NW (#SF = 26) increases the compressive Young’s Modulus about 14.6 – 14.84% and an increase of 5.22 – 8.32% is seen in tensile Young’s Modulus in the simulated temperature range. The physics behind this increase in Young’s Modulus can be explained by the change in bond nature [11,12,17] and intrinsic SF-induced stress [17]. Due to an overlap between SF-induced stress and surface stress, the atoms at the intersection of SF/free surface undergo a local deformation, as seen in Fig. 3b, and subsequently change the bond characteristics [17]. Also, the SFs disturb the local stress around them and generate a heterogeneous stress distribution. To illustrate the inhomogeneity, the longitudinal strain, $\varepsilon_z$, distribution for the relaxed structure is plotted in Fig. 10 for $T = 300$ K. The strain distribution changes around the SFs, and adding more defect to the system causes overlapping among the intrinsic stress. This consequently affects the bond length, which leads to variation of Young’s Modulus; bond length is proportional to $d^{4/3}$. In low temperature, i.e., 0 K, this overlapping causes an increase in compressive strain and a decrease in tensile strain, leading to strengthening (see [17]). However, with increasing temperature, the SF-induced strain can be relaxed by the thermal fluctuations, and more defects are needed to exceed the perfect structure. This phenomenon can be seen in Fig. 10 that illustrates the distribution of the longitudinal strain, $\varepsilon_z$, for NWs with various defect densities at $T = 300$ K. The strain distribution changes around the SFs, and adding more defect to the system causes overlapping among the intrinsic stress. This consequently affects the bond length, which leads to variation of Young’s Modulus; bond length is proportional to $d^{4/3}$. In low temperature, i.e., 0 K, this overlapping causes an increase in compressive strain and a decrease in tensile strain, leading to strengthening (see [17]). However, with increasing temperature, the SF-induced strain can be relaxed by the thermal fluctuations, and more defects are needed to exceed the perfect structure. This phenomenon can be seen in Fig. 10 that illustrates the distribution of the longitudinal strain, $\varepsilon_z$, for NWs with various defect densities at $T = 300$ K. Longitudinal strain does not show a specific pattern (e.g., ascending/descending) until #SF 6 and, subsequently, a drastic enhancement in Young’s Modulus cannot be observed (see Fig. 8c). However, a considerable increase in Young’s Modulus was observed when the number of SFs was increased to 13 (see Fig. 8c). This corresponds to a reduction in tensile strain and an increase in temperature, and loading type (compression/tension) were calculated and are shown in Figs. 8 and 9. Fig. 8 shows an increase in Young’s Modulus in tension/compression with increasing density of SFs in all simulated temperatures in comparison to the perfect counterpart. 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compressive strain; see Fig. 10d and e. This shows the direct effect of strain distribution on fluctuation in Young's Modulus. It is worth mentioning that this reasoning is not applicable to highly defective NW, given that in this case, overlapping SF-induced stress becomes large enough to locally transform the WZ to BCT at the SF/free surface intersection zones and make a heterogeneous NW with two polymorphs (WZ and BCT). Fig. 9 depicts the variation of critical stress vs. SF density at different temperatures. Tensile critical stress is smaller in the defective NWs in comparison to the perfect structure, whereas, despite the initial reduction in compressive critical stress, it gradually increases by raising the SF density and ultimately shows higher strength than the perfect NW; #SF = 26 in all temperatures. Comparing the compressive critical stress of the highly defective to the perfect NW shows a 26.08–34.05% increase in critical stress, which is a considerable strengthening. The compressive critical stress of low SF density is lower than the perfect structure in all temperatures. In NW with high SF density, the BCT polymorph appears at the intersection of SF/free surface, despite the fact that HX is the stable polymorph in compression; BCT is stable under tensile loading. Therefore, one requires more energy to transform this heterogeneous structure (WZ/BCT) to HX. The nucleation energy of high SF density in Table 1 verifies this hypothesis. In the tensile loading, the SFs shows an opposite trend: reduction in critical tensile stress for all SF density and temperatures. This is due to the fact that the intersection of SFs and the free surface can serve as an active site for crack nucleation.

4. Conclusions

In summary, this study covers the mechanical response of defective NWs under various defect density, temperature, and loading conditions. The results demonstrate that decorating an NW with equal-spaced SFs leads to a decrease in critical tensile stress in comparison to the perfect counterpart over a wide temperature range (100–500 K). However, it enhances the tensile Young's Modulus: a 7% enhancement with respect to the perfect structure. Modeling the same defected NW under compression results in about a 14% increase in compressive Young’s Modulus and about 30% improvement in compressive critical stress. This non-trivial result defies the prevailing notion that defects always play a dominant role in deteriorating the mechanical properties of the nanostructures. These findings potentially open a new route for the fabrication of durable and novel nano-energy generators assemblies. The physics behind this enhancement are multifaceted and can be explained by the change in bond strength, overlapping the intrinsic SF-induced stress fields and the interplay between SF and surface stress. Introducing the SFs along the c-axis produces a bamboo-like structure that shifts the nucleation site toward the middle of each segment and forms a barrier for the propagation of the new PT. These results suggest the possibility of arresting PT at the immobile SFs, which subsequently improves the compressive load carrying capacity of the highly defected NWs. Moreover, a novel stress relaxation and deformation mechanism was observed for these NWs. An increase in the density of SFs is accompanied by an increase in the mechanical energy storage capacity of the NW and results in activating the new mechanism to release the stored energy; the PT was arrested at the SFs, and the NWs relaxed its energy by forming a twin boundary. This unique stress relaxation has not been observed for the NWs, and it verifies the ability of defect engineering in altering the mechanical response of materials under different loading types. All these findings suggest a new route for the fabrication of high-strength, low-dimensional nanostructures. Additionally, the impact of defects on material properties is not only limited to the mechanical properties, and its imprint can be explored on other aspects of properties (e.g., catalytic, electric), which broadens...
material design space and stretches the designer’s flexibility in tuning the desired properties. More in-depth studies with ab initio or density functional theory (DFT) are required to shed light on the change in energy landscape as well as in bond strength. Developing a model for nucleation and phase propagation is desirable to illustrate the interaction between PT and SFs.

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