Nanodisturbances in Deformed Nanowires

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A new physical mechanism of plastic deformation in nanowires is suggested and theoretically described. This mechanism represents formation of near-surface nanodisturbances—nanoscopic areas of plastic shear with tiny shear vectors—in deformed nanowires. We calculated the energy characteristics for nanodisturbance formation and compared them with those for conventional dislocation generation. It is shown that the nanodisturbance deformation mode tends to dominate in Au nanowires deformed at high stresses and zero temperature.

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Defect structure evolution and plastic deformation processes in nanometer- and submicron-sized wires (hereinafter called nanowires) recently attracted tremendous attention motivated by their wide potential use in technologies; see, e.g., [1–14]. Of particular interest is the size effect on the deformation behavior of nanowires exhibiting a dramatic increase in strength with reduction of nanowire diameter. For instance, following experiments [2,5,6,13], metallic nanowires with a diameter of around 200–500 nm under compression show strength values highly exceeding (by 10–50 times) those of bulk materials with the same chemical composition. In order to explain superior strength of nanowires, Greer and Nix [5,6] suggested the idea of dislocation starvation. Within their model, preexistent dislocations move and rapidly disappear at nanowire free surfaces during the first deformation stage which makes a nanowire free from dislocations. Then, the second stage of deformation occurs at very high applied stresses needed to cause plastic flow of the defect-free nanowire. In the context discussed, there is great interest in understanding the fundamental physical mechanisms that govern plasticity in defect-free nanowires at the nanoscale level. Computer models [11,12] of plastic flow in initially defect-free nanowires showed that dislocations nucleate at free surfaces of mechanically loaded nanowires. The main aim of this Letter is to suggest and theoretically describe a new (alternative) mechanism of plastic deformation in defect-free nanowires. This mechanism represents formation of near-surface nanodisturbances defined as nanoscopic areas of plastic shear with tiny shear vectors formed near nanowire free surfaces. Such near-surface nanodisturbances are similar to ''bulk'' nanodisturbances [15–17] observed by *in situ* experiments [18] in grain interiors of special titanium alloys during plastic deformation.

Let us consider the process of plastic deformation in a single crystalline nanowire having initial shape of a long rectangular box with a square base having the sizes $d \times d$ [Fig. 1(a)]. In the situation where the nanowire is free from defects, its plastic flow can occur through conventional nucleation of dislocations at a nanowire free surface and their further glide across a nanowire cross section [Figs. 1(a)–1(e)] [11,12]. We think that plastic flow in the nanowire can occur in an alternative way through formation of near-surface nanodisturbances, nanoscopic areas of plastic shear with tiny shear vectors formed near nanowire free surfaces [Figs. 1(f)–1(j)].

Let us discuss details of this special deformation mechanism. They are illustrated in both a general three-dimensional view on a nanowire under tensile deformation in Figs. 1(f)–1(j) and a two-dimensional view on one of crystallographic planes of the nanowire in Figs. 1(k)–1(o). At the initial stage, an applied shear stress causes a ''momentary'' ideal (rigid-body) shear to occur along the nanoscale fragment *ABCD* of a nanowire cross section misoriented by 45° relative to the nanowire axis [Figs. 1(f), 1(g), 1(k), and 1(l)]. Such a shear is characterized by a tiny shear magnitude s and produces a generalized stacking fault *ABCD* having nanoscale sizes [Figs. 1(g) and 1(k)]. (In the theory of crystals, a generalized stacking fault is defined as a planar defect resulted from a cut of a perfect crystal across a single plane into two parts which are then subjected to a relative displacement through an arbitrary vector **s** (lying in the cut plane) and rejoined; see, e.g., [19,20].) The generalized stacking fault is bounded in the nanowire interior by a ''noncrystallographic'' partial dislocation CD characterized by a nonquantized (noncrystallographic) Burgers vector **s** with quite a small magnitude $s < b$, where b is the magnitude of the Burgers vector of a conventional ''crystallographic'' partial dislocation [Figs. 1(g) and 1(l)]. This defect configuration is called the near-surface nanodisturbance. At the following stage, the magnitude s continuously increases [Figs. 1(h) and 1(m)]. In parallel with the increase in s, the noncrystallographic partial can move. Then, the magnitude s reaches the magnitude b, and the nanodisturbance transforms into a conventional partial dislocation joint by a stable stacking fault (a generalized stacking fault with minimum energy) *ABCD* with the free surface

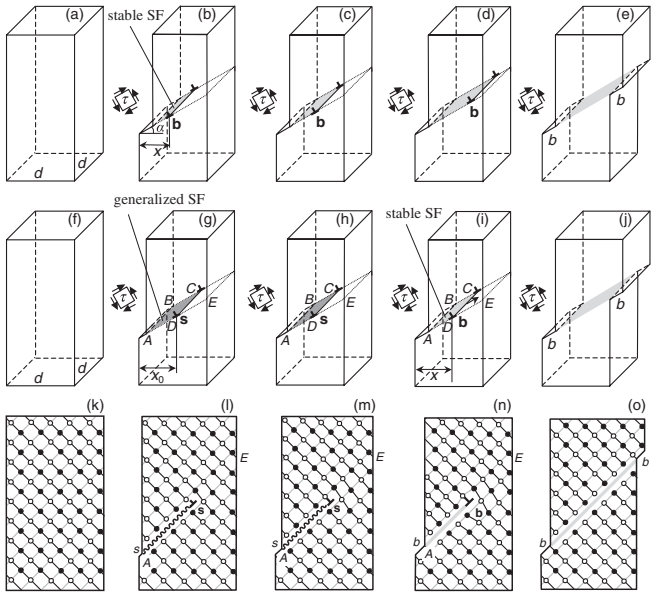

FIG. 1. Plastic deformation modes in nanowires. (a)–(e) Conventional partial dislocation slip. (a) Initial state. (b)–(e) Conventional partial dislocation with Burgers vector $\boldsymbol{b}$ generates at the first free surface (where a step with width b is formed) and slips towards opposite free surface. Stable stacking fault (SF) joins the dislocation and the first free surface. (f)–(j) Nanodisturbance deformation mode (three-dimensional view). (f) Initial state. (g) and (h) Immobile noncrystallographic dislocation is generated. Its Burgers vector magnitude s gradually increases from 0 to b, and a generalized stacking fault (gray region) is formed (and evolves in parallel with growth of s) between the dislocation and a nanowire free surface. (i) The partial dislocation transforms into a conventional partial dislocation (when s reaches the magnitude b of the Burgers vector of a conventional partial dislocation) and then moves towards the second free surface. (j) The final structure with two surface steps is formed. (k)–(o) Two-dimensional view on nanodisturbance deformation mode in a crystallographic plane (containing slip line AE) of a nanowire with a cubic elementary cell containing atoms of two sorts (full and open circles).

[Figs. 1(i) and 1(n)]. The conventional partial moves and disappears at the free surface [Figs. 1(j) and 1(o)].

Note that the near-surface nanodisturbances [Figs. 1(g)–1(i) and 1(l)–1(n)] in nanowires are similar to "bulk" nanodisturbances experimentally observed [18] in grain interiors of deformed titanium alloys. Such bulk nanodisturbances are bounded by loops of "noncrystallographic" partial dislocations and nucleate due to high shear stresses and dramatic decrease in some elastic constants [15–18]. As it will be shown below, formation of near-surface nanodisturbances occurs as a new deformation mode in nanowires [Figs. 1(g)–1(i) and 1(l)–1(n)] due to the nanoscale and free surface effects (causing the nanodisturbance stresses to be effectively screened in nanowires).

Let us calculate the energy characteristics of the new and conventional modes of plastic flow in nanowires in the example case shown in Fig. 1. Plastic shear occurs along a plane misoriented by angle α relative to the square base cross section (Fig. 1) of the nanowire under the action of the shear stress τ acting in this plane. The nanowire is supposed to be an elastically isotropic solid having the shear modulus G and the Poisson ratio ν. Within our model, a nanowire is subjected to a constant external stress. Formation of a nanodisturbance and evolution (in time) of its characteristics, s and x, represent the plastic response of the nanowire material to this mechanical creeplike test. The new deformation mode [Figs. 1(g)–1(i) and 1(l)–1(n)] is characterized by the change ΔW of the nanowire energy due to the nanodisturbance formation. The energy change ΔW (the difference between the energy of the nanowire with the nanodisturbance and that of the defect-free nanowire) consists of the four terms:

$$\Delta W = W_d + W_s + W_\gamma - A, \tag{1}$$

where W_d is the proper energy of the noncrystallographic partial dislocation (per its unit length), W_s is the free surface energy related to formation of free surface step(s) due to plastic shear across a nanowire section, W_γ is the generalized stacking fault energy, and A is the work spent to glide of the noncrystallographic partial.

The analytical expression for the proper energy W_d of the dislocation having a finite length in a rectangular nanowire is unknown. In this case, we approximately take W_d as the energy of infinite dislocation (per its unit length) in a semi-infinite solid near its plane free surface parallel with the dislocation line [21]. Also, following the standard approximation [7,22,23] used in calculation of the energy of dislocations in nanostructures, we suppose the energy W_d to be dependent on only the distance between the dislocation line and the nearest free surface. This distance is $\min(x, d - x)$, where x is the distance between the dislocation and the first free surface at which the dislocation is generated [Fig. 1(b)]. The dislocation disappears, and the second step at the second free surface generates, when the dislocation reaches this surface, that is, when $x = d - b$ [Figs. 1(e) and 1(j)]. In these circumstances, after some algebra, we find the following expression for the energy change ΔW per unit length of the dislocation:

$$\Delta W(x, s) = \frac{Ds^2}{2}\left(\ln\frac{\min(x, d - x)}{s} + 1\right) + \gamma_s s + \gamma_{\mathrm{gsf}}(s)x/\cos\alpha - \tau s x/\cos\alpha. \tag{2}$$

Here $D = G/[2\pi(1 - \nu)]$, γ_s is the specific energy of the free surface (per its unit area), $\gamma_{\mathrm{gsf}}(s)$ is the specific energy of the generalized stacking fault (dependent on s). The parameter x varies from b to $d - b$.

Note that the described approximation for the energy W_d is accurate enough. It is approved by our analysis (not shown here, because of limits in space) based on the known formula [24] of the energy of an edge dislocation in a thin plate, taking into account the screening effects of the two free surfaces of the plate. Following the analysis, the difference between the values of W_d calculated within

our simple model (Fig. 1) and that calculated by formula [24] is small (around 20% or lower). Also, real crystallography of Au nanowires suggests that a nanodisturbance should nucleate from a corner point and propagate across the rhombic slip plane {111}. Description and theoretical examination of this real situation are rather complicated and space consuming, while their results are very similar to those obtained in analysis of the simple model geometry (Fig. 1). In particular, the nanodisturbance deformation mode in the model and real geometries occurs in the nonbarrier way when the external stress is larger than a critical value τ_c and τ_c', respectively. According to our calculations, the difference between τ_c and τ_c' ranges from around 3% to 12%, depending on the nanowire size d (=10–50 nm). Also, the key conclusion (that the nanodisturbance deformation mode dominates over the conventional dislocation slip; for details, see below) of our examination is the same in both the model and real geometries. In these circumstances, for simplicity and shortness, in this Letter, we will consider the simplest geometry only (Fig. 1).

The energy change $\Delta W(x, s)$, given by formula (2), characterizes generation and evolution of a nanodisturbance. When $s = b$, formula (2) transforms to the expression for the energy change describing classical generation and glide of a lattice partial dislocation. In this context, analysis of expression (2) allows one to calculate the energy characteristics of both the new and classical deformation modes as well as to reveal the optimum way of the system evolution. Below, we performed such an analysis in the example case of Au nanowire with the following typical values of parameters: $G = 27$ GPa, $\nu = 0.44$, $\gamma_s = 1.48$ J/m^2 [21]. The gliding partial dislocation is chosen as an edge Shockley dislocation with Burgers vector magnitude $b = 0.166$ nm. The specific energy dependence $\gamma_{\mathrm{gsf}}(s)$, for the generalized stacking fault in Au, was simulated in Ref. [25]. With results [25], this dependence can be approximated by the following formula:

$$\gamma_{\mathrm{gsf}}(s/b) = \begin{cases} \frac{\gamma_m}{2}(1 - \cos\frac{2\pi s}{b}), & 0 \le s/b < 1/2, \\ \frac{\gamma_m + \gamma_0}{2} - \frac{\gamma_m - \gamma_0}{2}\cos\frac{2\pi s}{b}, & 1/2 \le s/b < 1. \end{cases} \quad (6)$$

Here γ_m and γ_0 are the maximum and minimum values of $\gamma_{\mathrm{gsf}}(s)$, corresponding to unstable and stable configurations of the generalized stacking fault. For Au, one has $\gamma_m \approx 0.09$ J/m^2, $\gamma_0 \approx 0.031$ J/m^2 [25]. Using formula (2), we calculated the energy maps $\Delta W(x, s)$, for Au nanowire with the size $d = 10$ nm, the angle $\alpha = 45°$ and the following values of the external stress $\tau = 0.8$ and 1.9 GPa [Figs. 2(a) and 2(b)]. These maps allow us to analyze the system evolution in the parameter space (x, s) for both new and classical deformation modes.

Within our model, the final defect configuration in a deformed Au nanowire is specified by the parameter pair $(x = d - b,\ s = b)$ and corresponds to the upper right corner of the energy map shown in Fig. 2. In this case,

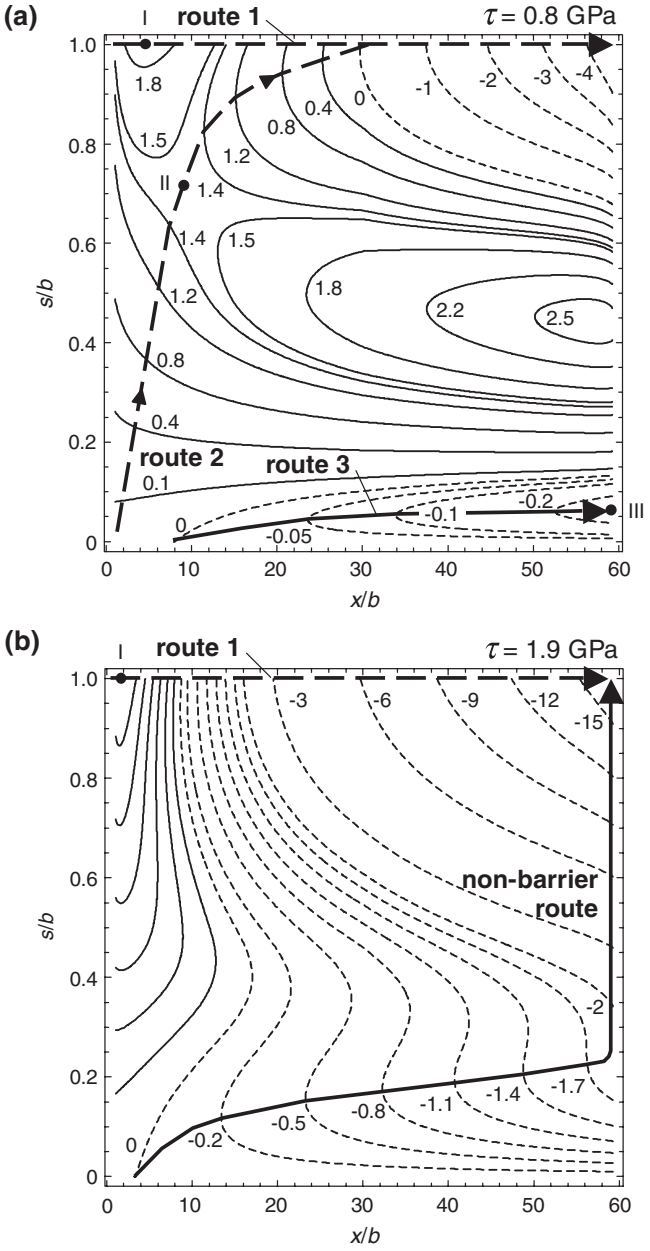

FIG. 2. Maps of the energy change $\Delta W(x, s)$ in the case of Au nanowire with the size $d = 10$ nm and $\alpha = 45°$ under the external shear stress (a) $\tau = 0.8$ GPa and (b) 1.9 GPa. The values of ΔW are given in units of Db^2.

the classical deformation mode corresponds to the arrowed route 1 at the upper part of the map. The route 1 is characterized by the energy barrier whose height is given by the energy value at point I. The main contribution to the barrier height is related to formation of a free surface step. Therefore, the height is almost insensitive to the stress. Also, there is the route 2 corresponding to the nanodisturbance deformation mode. For comparatively low values of the stress τ [Fig. 2(a)], function $\Delta W(x, s)$ has a saddle point II at the route 2, where the energy value is lower than that at point I. In this case, the nanodisturbance deformation mode (route 2) is characterized by lower

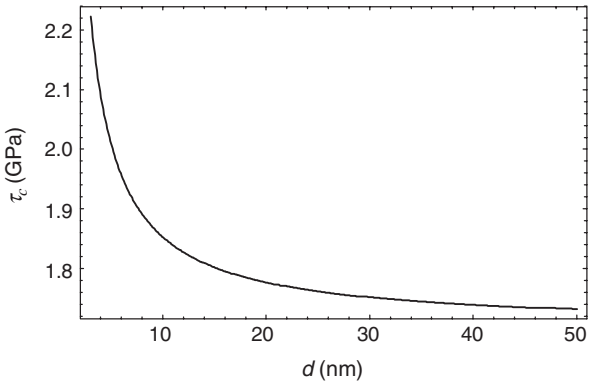

FIG. 3. Dependence of the critical stress τ_c (the smallest stress at which the nanodisturbance deformation mode occurs in the nonbarrier way in Au nanowire) on the nanowire size d.

energy barrier, compared to the classical deformation (route 1). The determination of saddle point energies [Fig. 2(a)] suggests that the results of our model may be applied in the future to related, thermally activated overcoming mechanisms that control mechanical properties of nanowires.

In this Letter, for definiteness, we will consider a zero temperature situation. For comparatively low values of the stress τ [Fig. 2(a)], the system at zero temperature evolves by the route 3 to a state with the lowest energy [point III specified by $x \sim 60b$ and $s \sim 0.05b$ in Fig. 2(a)] and no barrier. For a low stress level [Fig. 2(a)], the system at zero temperature never actually gets to the final configuration of $x = d - b$ and $s = b$. For large values of the stress τ, the nanodisturbance mode occurs in the nonbarrier way and gets to the final configuration at zero temperature, in contrast to the classical deformation [see Fig. 2(b)]. In this case, the Au nanowire is unstable relative to the nanodisturbance deformation. The energy maps $\Delta W(x, s)$ are very similar, for Au nanowires with the size d ranging from 10 to 300 nm. That is, the nanodisturbance deformation is expected to play the dominant role in ideal Au nanowires with widely ranged sizes. The critical stress τ_c (the smallest stress at which the nanodisturbance deformation occurs in the nonbarrier way) shows a moderate sensitivity to d (Fig. 3).

Thus, a new deformation mode—deformation through formation and evolution of near-surface nanodisturbances associated with nanoscale ideal shear—can occur in strained nanowires due to the nanoscale and free surface effects. With results of our calculations of its energy characteristics, the nanodisturbance deformation mode dominates (over conventional dislocation generation and glide) in ideal Au nanowires at high stresses and zero temperature. Also, this fundamentally new mechanism of nanoscale deformation is expected to be effective in composite solids containing nanowires.

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