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Surface-induced structural transformation in nanowires

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ABSTRACT

One of the unique features of nanomaterials is that they have large surface-to-volume atom ratios compared to bulk materials. The intrinsic compressive stress along the nanowire axis can be as large as tens of GPa, and spontaneous reorientation or phase transformation may occur in order for the nanowires to return to the low-energy state. Upon tensile loading, the nanowires can revert back to the original high-energy orientation or phase without introducing any defects. Two mechanisms are mainly involved in the deformation: (1) twinning/detwinning and (2) stress-induced martensitic phase transformation (MT)/inverse MT. Generally, this surface-induced behavior can only occur at a temperature higher than the critical temperature, T_c, due to the energy barrier for structural transformation. As a result, ordinary nanoscale metals can exhibit pseudo-elasticity and shape memory effects previously only observed from special alloys such as nickel titanium (NiTi). These nanowires have the predicted recoverable strain on the order of 40%–70% which is much larger than that of bulk NiTi (5%–10%), but have extremely low energy dissipation (2% for W nanowires, for example). Surface-induced structural transformation has been observed from fcc, bcc, and hcp single-element metal nanowires, intermetallic alloy nanowires, multilayered and core-shell composite nanowires, and even oxide and nitride compound semiconductor nanowires. This unique phenomenon enables the design of novel and flexible nanoelectromechanical systems (NEMS) having potential applications in nanomanipulators, energy storage, sensors, switches, and so on. We will review the breakthrough and development in this field in the past ten years, mainly focusing on the physical mechanisms and dominant factors governing this spontaneous structural transition. Future developments will also be discussed.

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1. Introduction

1.1. Surface energy and surface stress in nanomaterials

Nanostructured materials have unique properties and extensive research in the past decade, and have spurred the development of novel products such as nanoelectronic devices [1–3], energy conversion and storage systems [4–10], and biomedical diagnostic devices and sensors [11,12]. The large surface-to-volume ratio with a magnitude of 10^6–10^9 m^{G-1} [13,14] is one of the fundamental characteristics of nanomaterials. Since there are more surface atoms on nanomaterials than their bulk counterparts, dangling atoms on the surface increases the surface energy and the broken atomic symmetry on the surface induces surface stress [15,16]. The surface energy and surface stress are in fact the dominant thermodynamic parameters governing the structural stability of nanomaterials.

In the context of thermodynamics, the surface energy is the reversible work needed to create a new surface per unit area and is a scalar, whereas the surface stress is a second-order tensor representing the reversible work per unit area needed to elastically stretch a pre-existing surface [16]. Accordingly, the surface stress tensor, $\tau_{\alpha\beta}$, can be obtained by partially differentiating the surface energy with respect to the strain components. Assuming that a homogenous strain $\varepsilon_{\alpha\beta}$ ($\alpha,\beta\in(x,y)$) is applied to the surface plane, the stress tensor can be expressed as [16,17]:

$$\tau_{\alpha\beta} = A_{\mathrm{surf}}^{-1}\partial(\gamma_{\mathrm{surf}}A_{\mathrm{surf}})/\partial\varepsilon_{\alpha\beta} = \partial\gamma_{\mathrm{surf}}/\partial\varepsilon_{\alpha\beta} + \gamma_{\mathrm{surf}}\partial A_{\mathrm{surf}}/\partial\varepsilon_{\alpha\beta}, \qquad (1)$$

where A_{surf} denotes the surface area of the system and γ_{surf} is the surface energy per unit area. The first term in Eq. (1) denotes the change in the surface energy with respect to strain due to the variation in the atom density on the surface and the second term is associated with the variation in the surface area upon mechanical loading. Since $dA_{\mathrm{surf}} = A_{\mathrm{surf}}\delta_{ij}d\varepsilon_{ij}$ (where δ_{ij} is the Kronecker delta) [16], Eq. (1) can be rewritten as:

$$\tau_{\alpha\beta} = \partial\gamma_{\mathrm{surf}}/\partial\varepsilon_{\alpha\beta} + \gamma e\delta_{ij}. \qquad (2)$$

In a liquid, atoms are free to move and when the surface area is altered, interior atoms can migrate outwards to compensate and vice versa. Consequently, the atom density on the surface does not change and the surface energy γ_{surf} has a constant value. Only the second term in Eq. (2) remains and so the surface stress is equivalent to the surface energy in a liquid. However, in a solid, diffusion is restricted normally and when the surface atomic density is changed under an external load, the surface energy is altered. Both terms in Eq. (2) contribute to the surface stress and so the surface stress contains an additional term besides the surface energy having the same order of magnitude. On a clean surface, γ_{surf} is always positive while $\partial\gamma_{\mathrm{surf}}/\partial\varepsilon_{ij}$ can be positive or negative. As a result, the surface stress $\tau_{\alpha\beta}$ can be positive or negative indicative of tensile or compressive interaction, respectively. When some gaseous molecules adsorb on the surface, the bonding states of the surface atoms will be changed thereby further modifying the surface energy and stress.

The surface energy and surface stress are usually orientation-dependent and anisotropic. Although it is difficult to measure these two parameters experimentally, they have been predicted by theoretical methods such as the embedded atom method (EAM) [18–22], modified embedded atom method (MEAM) [20,21,23–25], surface embedded atom method (SEAM) [26], density function theory (DFT) [27–35], and tight-binding (TB) [21]. Table 1 lists the results of typical face centered cubic (fcc) metals and only {1 0 0} and {1 1 1} planes are shown as examples. Although there are distinct differences between the results obtained from different theoretical approaches, there is a consistent trend. That is, the {1 1 1} surfaces have the lowest energy due to the closely packed atom configuration in fcc metals. This often leads to a preferred surface or faceting in as-grown materials [36–46]. Tensile surface stress is usually observed and it is balanced by the internal compressive stress. The cases for three typical nanomaterials are schematically shown in Fig. 1. Specifically, a two-dimensional (2D) nanoscale thin film experiences in-plane biaxial stress [Fig. 1(a)], a one-dimensional (1D) nanowire is subjected to triaxial stress with a larger component along the wire axis [Fig. 1(b)], and a zero-dimensional (0D) nanoparticle has hydrostatic stress [Fig. 1(c)] [21]. All the non-zero components of the compressive stress tensor are proportional to the surface stress but inversely proportional to geometric parameters such as the film thickness, wire width, or particle diameter. Taking into consideration the values of surface stress listed in Table 1, the surface-induced compressive stress has a magnitude of GPa or even tens of GPa when the size is on the nanometer scale. Under these conditions, the structural stability of nanomaterials may be changed significantly leading to structural transformation.

1.2. Size-dependent structural stability of nanomaterials

Surface reconstruction is one of the typical structural changes in response to the existence of high-energy planes and has been observed from semiconductors [47–50] and metals [51–53]. On the (1 0 0) oriented surfaces of fcc metals such as Ir, Pt, and Au, the surface layer with a thickness of several atomic layers contracts and reconstructs into a hexagonal close-packed lattice. This is in contrast to the square lattice beneath in order to minimize the system energy [32,54–56]. If the bulk materials with high-energy surfaces are thinned to an ultra-thin scale, for example, several atomic layers, all the atoms can experience the existence of surface and the structure change should be throughout the sample. Kondo et al. [57] provided experimental evidence. In their experiments, a (0 0 1) Au film was mounted on a holey carbon film and thinned by intense electron beam irradiation in an ultra-high vacuum electron microscope. When the central area was thinned to 2–3 nm corresponding to about 8 atomic layers, the (0 0 1) thin film spontaneously transformed into a (1 1 1) one [57] on account of surface energy minimization driven by compressive stress. More evidence about other transition metals including the 4d and 5d groups was demonstrated by molecular dynamics (MD) simulation [58]. Hasmy and Medina [58] reported that the strain energy