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Thermal stability and spontaneous breakdown of free-standing metal nanowires

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ABSTRACT

We present a model for vacancy-mediated spontaneous breakdown of free-standing monatomic nanowire based on exclusively random, thermally activated motion of atoms. The model suggests a new two-step vacancy-mediated mechanism for nanowire rupture compared to the more complex three-step hole-mediated mechanism driving the disintegration of nanowire on crystalline surface. It also demonstrates that a free-standing nanowire breaks down much more rapidly than a nanowire on a substrate, because it cannot experience the stabilizing effect of the nanowire/substrate interactions. The rupture mechanism includes single atomic vacancy generation, preceded by appearance of weakly bonded active atoms. The analysis of the simulation data indicates that the active atoms act as a precursor of vacancy formation. These two successive events in the temporal evolution of the nanowire morphology bring the free-standing nanowire into irreversible unstable state, leading to its total disintegration.

The present study also manifests an unexpected substantial increase of the nanowire lifetime with diminishing the strength of the atomic interactions between the nanowire atoms. The simulation data reveal three energy regions where a large oscillatory variation of nanowire lifetime is realized. The first region of strong atomic interactions is characterized by tight nanowire rigidity and short lifetime. The next, second region in the consecutive step-down of the attractive interatomic force is characterized by generation of wave-shaped morphology of the atomic chain, enhanced flexibility and dramatic increase of nanowire lifetime. In the last, third region, further weakening of the interactions returns the nanowire again to unstable, short-lifetime state. The observed phenomenon is considered as a "stick-like" to "polymer-like" transition in the nanowire atomic structure as a result of interaction energy variation. The enhanced flexibility reduces the nanowire free energy since it favors and facilitates the rate of entropy propagation in the atomic chain structure. The observed phenomenon opens a way for a new type atomic scale control on the thermal stability of both free-standing nanowire and nanowire on crystalline substrate. The present study also extends the validity of the three-step breakdown mechanism of nanowire on crystalline substrate to the specific case of thermally activated free-standing nanowire rupture not affected by any external forces.

1. Introduction

Metal atomic nanowires hold special attention in contemporary materials science because of their great scientific and technological importance. These low-dimensional linear structures excite also remarkable academic curiosity in relation to their structure, stability, and quantum properties [1–12]. The exotic physical features of metal nanowires also provide a challenging background for a large number of applications in nanoelectronics, optics and catalysis. Being a cutting-edge problem in the nanoscale physics, the theoretical and experimental studies on the thinnest nanowires have hitherto been mainly focused on the question of how to create nanowires [1–3,9]. Considerably less attention has been paid to the nanowire stability, rupture and complete disintegration [11,12]. That is why, the present study deals with the problem of how a single nanowire breaks down spontaneously, exclusively as a result of the thermal motion of the atoms in it.

Recently, a new physical model for spontaneous, hole-mediated breakdown of monatomic metal nanowires on crystal surfaces has been suggested [12]. The physical scenario of the breakdown process implies three consecutive steps of nanowire rupture including:

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(i) formation of active atoms, (ii) generation of single atomic vacancy and (iii) evolution of the single vacancy into a two-vacancy cluster (called hole). In all these steps involved into the nanowire rupture, illustrated in Fig. 1, the influence of the substrate is significant. The substrate affects the nanowire stability in different ways. It can stabilize or, in contrast, facilitate the nanowire breakdown depending on its anisotropy, softness of the surface potential, lattice misfit between substrate and nanowire, etc. Special attention has to be paid to the role of incommensurability with the crystalline surface. In some cases, the lattice mismatch could be crucial for the nanowire breakdown and its total disintegration. The contribution of these simultaneously acting, competing effects is controlled by the substrate/nanowire interface energy minimization. Since a large number of experiments deal with the nanowire features on a substrate, in the present study we discuss the thermal properties of a free-standing monatomic nanowire in vacuum where the influence of the substrate is entirely avoided. In this way, we assess more clearly the impact of the atomic interaction potential on the nanowire stability and reveal the nanowire breakdown scenario in the absence of external field. Hence, we focus our study on the following questions: (i) Could the model of vacancy- and hole-mediated nanowire rupture, valid for nanowire on surface, be extended to a free-standing nanowire? (ii) What is the influence of the strength of the interactions between the nanowire atoms on the nanowire morphology, atomic structure and stability? (iii) How does the nanowire flexibility affect the nanowire thermal stability? The answers to these questions could contribute to a better understanding of the fundamental mechanism of monatomic nanowire breakdown and its complete disintegration which is a matter of great importance in contemporary interface materials science [1–7].

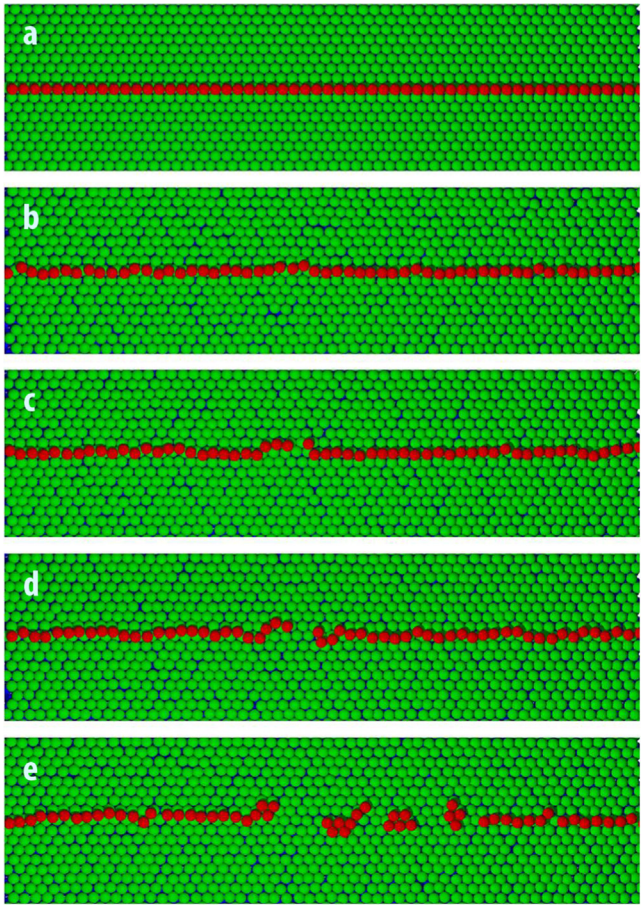

Fig. 1. Hole-mediated breakdown of a nanowire on crystalline surface. The time evolution reveals multistep rupture mechanism leading to total nanowire disintegration. (a) Initial configuration. (b) Formation of active sites (precursors) at 200 MCS. (c) Generation of single vacancy at 500 MCS. (d) Generation of hole (double vacancy) at 2800 MCS. (e) Formation of atomic clusters at 9900 MCS (after Michailov and Kashchiev [12]).

2. Physical and computational models

The physical model in the present study is designed to reveal the time evolution of free-standing monatomic Cu chain in vacuum at constant temperature T. The atoms which are exposed to thermal fluctuations only are bound via interacting potential. The computational model is grounded on classical canonical Monte Carlo (MC) sampling with many-body Tight Binding Second Moment approximation (TB SMA) potential between atoms [13–16]. In this approach, the total interaction energy E_i of atom i in the system is expressed by

$$E_i = E_i^r + E_i^b, \tag{1}$$

with E_i^r and E_i^b being, respectively, the repulsive and attractive energy terms. Explicitly, E_i is given by [13]

$$E_i = \sum_{j, r_{ij} < r_c} A \exp\left[-p\left(\frac{r_{ij}}{r_0} - 1\right)\right] - \sqrt{\sum_{j, r_{ij} < r_c} \xi^2 \exp\left[-2q\left(\frac{r_{ij}}{r_0} - 1\right)\right]} \tag{2}$$

where r_{ij} is the distance between atoms i and j, r_0 is the nearest-neighbor atomic distance of the corresponding pure metal, A and p are energy- and compressibility-related free parameters, and r_c is the cutoff distance for the interaction. The first term in Eq. (2) is a Born–Meyer type ion–ion repulsion and the second term is the bond energy term, obtained in the form of the second-moment approximation of the electron density of states [13]. In Eq. (2), ξ is an effective hopping integral and $q$describes its dependence on the relative interatomic distance. In general, the expression for E_i^b, can be considered as a sum over the local electronic charge density induced at site i from the atoms at site j. Hence, ξ is expected to be sensitive to the number of surrounding atoms in all space directions. The energy calculation is performed over all atoms within a sphere having radius 3 times the Cu–Cu nearest-neighbor distance in the bulk crystal. The values of the hoping integral ξ and all related parameters A,p, and q in Eq. (2) are taken from [13,15]. The statistical distribution in our model is canonical, i.e., ensemble with constant number of particles at fixed temperature and volume [16]. In equilibrium, the system energy reaches its minimum and fluctuates around a constant value. Full lattice dynamics of all nanowire atoms ensures complete relaxation of the system. All simulations are grounded on three-dimensional continuous space model, i.e., nanowire atoms are able to change their positions in all space directions with a step of 0.05 units of the lattice constant. The initial nanowire configuration is a perfectly ordered linear monatomic chain with periodic boundary conditions along the chain axis. All simulation data are averaged over 50 runs with single nanowire for each temperature and each value of the attractive term in the interaction potential in Eq. (2). The nanowire length is 76 atoms. The variation of the nanowire morphology and its atomic structure are monitored by a series of successive snapshots taken at every 10 Monte Carlo Steps (MCS). In all simulations, the nanowire follows the classical thermodynamic pathway towards equilibrium of an ensemble of atoms by minimization of the system energy via clustering. Complete simulation details are described elsewhere [12,15].

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