Thermal Rupture of Monatomic Metal Nanowires

M Michailov and D Kashchiev
Institute of Physical Chemistry, Bulgarian Academy of Sciences, “Acad. G. Bonchev” Str., Block 11, 1113 Sofia, Bulgaria
E-mail: mike@ipc.bas.bg

Abstract. The present study deals with the problem of thermal stability and rupture of metal nanowires, considered here as a monatomic chain located on an atomically smooth crystalline substrate. Based on a recently developed Monte Carlo computational model, the simulation results reveal a scenario of nanowire breaking via formation of atomic vacancies. Depending on temperature, the fluctuations in the positions of the nanowire atoms generate wave-shaped nanowire configurations with specific active sites for breaking. This process is followed by formation of one-atom vacancies in the nanowire. Their overgrowth into vacancies of two, three and more atoms leads to permanent nanowire rupture and, hence, to loss of the nanowire electronic and other physical properties. The time evolution of the atomic-scale nanowire morphology and breaking mechanism are discussed in detail. The proposed model of nanowire rupture sheds light on the general problem of thermal stability of artificial atomic structures on crystal surfaces and their application to electronic and other devices with exotic physical features.

1. Introduction
Metal nanowires are of great technological importance due to their exotic physical properties. In the same time these systems excite remarkable academic curiosity because of the physics behind their reduced dimensionality and resulting quantum behavior [1]. Being at the cutting edge of nanoscale science, the theoretical and experimental studies of this problem are generally focused on the issue of “how to create nanowires” [1-3]. Considerably less attention has been paid to the thermal stability and rupture of these structures [4-6]. That is why, the present work deals with the opposite issue of “how a nanowire destroys itself without external influence”. Focusing our study on that, we discuss the kinetic behavior of a monatomic metal nanowire (i.e. a chain of single metal atoms) located on an atomically smooth crystal surface. We investigate the nanowire atomic morphology and the probabilities of one- and two-atom vacancy formation in the nanowire.

2. Physical and Computational Model
The physical model in the present study is designed to represent a flat step-free atomically smooth crystal surface with a monatomic chain of the same material placed on it. As a model system we have chosen the Cu(111) surface with chain of 57 aligned Cu atoms on top. The initial system configuration is shown in figure 1a and is that of a perfectly ordered fcc(111) crystal surface with an infinite atomic chain on it because of imposed periodic boundary conditions. The system size in the corresponding space dimensions is $57 \times 33 \times 5$ lattice units.
The computational model is grounded on classic Monte Carlo (MC) sampling with many-body tight-binding second-moment approximation potential between interacting atoms [7]. In this approach, the total cohesive energy $E_i$ of atom $i$ in the system is expressed by

$$E_i = E'_i + E^b_i,$$

where $E'_i$ and $E^b_i$ being, respectively, the repulsive and attractive energies. The first energy is given by [7]

$$E'_i = \sum_{j, r_{ij} < r_c} A_{\alpha\beta} \exp \left[ -p_{\alpha\beta} \left( \frac{r_{ij}}{r_{\alpha\beta}} - 1 \right) \right]$$

and

$$E^b_i = -\sum_{j, r_{ij} < r_c} \xi_{\alpha\beta}^2 \exp \left[ -2q_{\alpha\beta} \left( \frac{r_{ij}}{r_{\alpha\beta}} - 1 \right) \right]$$

Here $\alpha$ and $\beta$ denote the chemical nature of atoms, $r_{ij}$ is the distance between atoms $i$ and $j$, $r_{\alpha\beta}^0 = (r_{\alpha\alpha} + r_{\beta\beta})/2$ if $\alpha \neq \beta$, $r_{\alpha\alpha}$ and $r_{\beta\beta}$ are the nearest-neighbor atomic distances of the corresponding pure metals, $A_{\alpha\beta}$ and $p_{\alpha\beta}$ are energy and compressibility related free parameters, and $r_c$ is the cutoff distance for the interaction. The energy $E^b_i$ is the band energy obtained in the form of the second-moment approximation of the electron density of states and is given by [7]

Here $\xi_{\alpha\beta}$ is an effective hopping integral and $q_{\alpha\beta}$ describes its dependence on the relative interatomic distance. In general, $E^b_i$ can be considered as an expression that represents a sum over the local electronic charge density induced at site $i$ from atoms at site $j$. Hence, $\xi_{\alpha\beta}$ is expected to be sensitive to the number of surrounding atoms. The energy calculation is performed over all atoms within a sphere having radius 3 times the Cu nearest-neighbor distance. The values of the hoping integral $\xi_{\alpha\beta}$ and all related parameters $A_{\alpha\beta}$, $p_{\alpha\beta}$, and $q_{\alpha\beta}$ in Eqs. 2 and 3 are taken from [7,8]. These values are consistent with the overall thermodynamic behavior of the system, since they reproduce basic physical characteristics of Cu crystal such as melting point, evaporation energy, elastic constants, etc.

The statistical distribution applied is canonical, i.e. ensemble with constant number of particles at fixed temperature [9]. At equilibrium, the system energy assessed over all atoms by Eq. 1 reaches its minimum and fluctuates around a constant value. Full lattice dynamics of both substrate layer and nanowire ensures complete relaxation of the system. The time evolution of the system is examined by a series of successive snapshots and pair-distribution function analysis. Complete simulation details are described elsewhere [10].

3. Time Evolution and General Scenario of Nanowire Rupture

In general, various parameters such as the temperature, type of atomic bonding to the substrate, crystallographic orientation, lattice mismatch between substrate and nanowire and elastic strain have an impact on the nanowire lifetime and rupture. In the present study, based on MC simulation experiments, we focus our attention exclusively on the significant role of thermal fluctuations. These fluctuations cause changes in the morphology of the atomic chain and result in a loss of essential
nanowire physical properties. To that extent, detailed analysis of our model system reveals different consecutive stages in the general scenario of nanowire time evolution, stability and rupture. At constant non-zero temperature, the nanowire tends to minimize its free energy by the thermal fluctuations in the positions of its building atoms. The nanowire develops a wave-shaped atomic morphology, the waves having clearly manifested maxima and minima (figure 1a). At a given critical value of the fluctuation amplitude, the atom thermal energy exceeds the interatomic binding energy and the nanowire breaks down (figure 1b). The breakdown is defined as the formation of a one-atom vacancy.

**Figure 1.** Breaking scenario of monatomic nanowire (red balls) on fcc(111) crystal surface (green balls) at 300 K. (a) Formation of active sites on the nanowire as a result of thermal fluctuations in the system. The wave-shaped nanowire geometry leads to weakening of the binding between the atoms at the wave maxima and minima. (b) Formation of one-atom vacancy and temporary nanowire rupture provided the nanowire discontinuity is restored via a random filling of the vacancy by an atom belonging to the nanowire.

Detailed time evolution and snapshot analysis suggests that the locus of rupture is the atomic position at the wave maximum or minimum (figure 1). Being considered as an active site, this special position is particularly significant, because it corresponds to weaker bonding of the atom occupying it. As seen in figures 1a and 1b, the nanowire is populated with a number of active sites on which a next generation of one-atom vacancies is very likely. The creation of such a vacancy results in breakdown, for example, of the nanowire conductivity and therefore loss of the respective electronic properties. It is essential to point out that the generation of a one-atom vacancy is not a process that irreversibly changes the nanowire morphology and integrity. Indeed, the vacancy can be filled up again by a randomly walking adatom that has been already detached from the chain. This process has been observed regularly in our MC experiments at sufficiently elevated temperatures. Hence, the nanowire could restore its integrity after a certain time. Since the formation of the first one-atom vacancy does not necessarily lead to permanent rupture, we consider this event as a step preceding the final stage of nanowire destruction.

The probability $P_v(t)$ of appearance of at least one vacancy in the nanowire until time $t$, defined as:

$$P_v(t) = \frac{N(t)}{N_{tot}}$$

(4)

is one of the parameters that characterizes the temporary nanowire rupture at a certain temperature. Here $N(t)$ is the number of nanowires possessing at least one vacancy until time $t$, and $N_{tot}$ is the total
number of nanowires studied. The statistical analysis of over $N_{tot} = 50$ nanowires at temperature $T = 300$ K resulted in the $P_v(t)$ curve shown in figure 2. The existence of two nanowire states is clearly seen in the figure: while at time $t < 200$ MC steps the nanowire is vacancy-free and thus stable, for $t > 200$ MC steps it is already unstable with respect to rupture. Naturally, the value of the time at which the nanowire loses its stability is a temperature function and also depends on the physical properties of materials (atomic bounding with the substrate, lattice misfit, crystallographic orientation, nanowire thickness, etc.).

![Figure 2](image)

**Figure 2.** Time dependence of the probability to form at least one atomic vacancy. Initial (left inset) and final (right inset) states of the nanowire atomic morphology are shown.

The later stage of nanowire evolution leads to irreversible breaking. During that stage the system is in a state in which the probability of filling up the nanowire vacancy is practically nil. This state is a result of generation of a larger vacancy containing more than one atomic vacancies. Our simulations showed that for a vacancy built-up even of two atomic vacancies, the event of nanowire integrity recovering is almost unlikely. The process of generation of one- and many-atom vacancies is visualized in figures 3a and 3b, respectively. It is worth pointing out that the formation of a two-atom vacancy is always preceded by the birth of a one-atom vacancy growing into a larger vacancy. The one- and two-atom vacancies shown in figure 3 originate, respectively, from active sites and one-atom vacancies shown in figure 1b. Therefore, both of these act as precursors for nanowire rupture.

![Figure 3](image)

**Figure 3.** (a) Single two-atom vacancy in a permanently ruptured nanowire; (b) One- and two-atom vacancies formed consecutively at three different active sites in the nanowire.
The curves in figure 4 depict the time dependences of the probabilities of appearance of at least one atomic vacancy and at least one two-atom vacancy. The shift of the latter with respect to the former reveals that at least one two-atom vacancy is born at a moment (ca. 1700 MC steps) when at least one atomic vacancy is already generated with certainty. The coexistence of one- and many-atom vacancies is seen in figure 3b. Inasmuch as $P_v$ is a temperature function, the shift magnitude opens up a way to control temperature-dependent time intervals for simultaneous generation of differently sized vacancies. This shift relates to the problem of the temperature limits of temporal or permanent break down of the nanowire electronic or other properties.

![Figure 4](image)

**Figure 4.** Time dependences of the probabilities to form at least one atomic vacancy and at least one two-atom vacancy. The inset represents an irreversibly growing vacancy.

A similar behavior was observed for nanowires constituted of two, three and more monatomic chains. Since the nanowire is wider, however, the formation of waves is less favorable with respect to that of a monatomic chain. In that case the active sites are local nanowire narrowing due to atomic roughening of the nanowire steps. The nanowire rupture occurs when the narrowing initiated at one of the nanowire steps becomes greater than the nanowire width. This process is manifested in figure 5 which illustrates the time evolution of a nanowire having three monatomic chains.

![Figure 5](image)

**Figure 5.** Consecutive snapshots illustrating the rupturing scenario of a nanowire of three monatomic chains (red balls) on fcc(111) crystal surface (green balls) at 300 K. The rupture occurs at a nanowire narrowing formed at a step of the nanowire.
Detailed snapshot analysis reveals another important effect related to the anisotropy of the substrate surface on which the nanowire is placed [10]. In the case of nanowires with width of more than about four atomic diameters, the nanowire narrowing beginning at B-type steps are greater than those beginning at A-type steps, figure 6. These two types of steps exist because of the specific crystallographic anisotropy of the fcc(111) surface and are illustrated in figure 6 (middle panel). This anisotropy leads to a different step free energy, relaxation ability, and diffusion barrier for displacement of atoms in directions A and B (figure 6) [11]. That is why, the roughing of B-steps costs less energy compared to that of A-steps. Because of symmetry reasons this effect does not exist on the cubic (100) surface. Therefore, the breaking process is not symmetric and depends on the substrate surface orientation through the anisotropy of the surface dynamics in different directions. It is important to note that the observed difference disappears at high enough temperatures where the diffusion energy of atoms belonging to the steps is higher than the energy barrier for perpendicular translation in both directions (see figure 6, right panel).

![A-step and B-step on fcc(111) crystal surface](image)

**Figure 6.** Anisotropy of thermal fluctuations of nanowire on fcc(111) substrate surface. At low temperature, $T = 300 \, \text{K}$, the B-step fluctuations are clearly pronounced in contrast to those of the opposite A-step. Increasing the temperature to $T = 400 \, \text{K}$, this anisotropy disappears because of the higher atom energy. The atomic configurations of A- and B-steps are presented in the middle panel of the figure.

4. Conclusion

The present study provides insight into thermal behaviour and structural evolution of monatomic metal nanowires homoepitaxially grown on crystal surfaces. The physical model considered outlines a general scenario of nanowire rupture as a three-step process of formation of vacancies. The first two steps involve the generation of rupture precursors (active sites and one-atom vacancies), and the last step is the actual formation of irreversibly growing vacancies of two and more atoms. This scenario is grounded on the observation that an atomic vacancy appears only when an atom at an apex of the wave-like nanowire leaves its place by attaching itself to one of the two nanowire steps. It is thus solely at a nanowire apex that an atom is active with respect to atomic vacancy formation. Before becoming active, the atom is unable to vacate its place in the nanowire, i.e. it is passive with respect to such a vacancy formation. Therefore, an atomic vacancy is born in two steps: first, a passive atom becomes an active atom by arriving at a nanowire apex owing to the undulatory motion of the whole nanowire, and second, this already active atom vacates its place by detaching itself from the nanowire. After that and this is the third and final step in the overall process of nanowire rupture, the so-born vacancy grows irreversibly. Detailed theoretical analysis on each step in the presented nanowire breaking model, including temperature dependence of rupture, probability distribution of vacancy...
cluster generation, lifetime and the impact of lattice mismatch between substrate and nanowire is in progress.

References

[1] Agrait N, Levy-Yeyati A and van Ruitenbeek J 2003 Phys. Rep. 377, 81
[2] Tersoff J and Tromp R 1993 Phys. Rev. Lett. 70, 2782
[3] Tosatti E, Prestipino S, Kostlikeir S, Corso A and Tolla F 2001 Science 291, 288
[4] Jelinek P, Perez R, Ortega J and Flores F 2003 Phys. Rev B 68, 085403
[5] da Silva E Z, da Silva A R J and Fazzio A 2001 Phys. Rev. Lett. 87, 256102
[6] Liu H, Jiang E, Bai H, Wu P, Li Z and Sun C 2008 Journal of Computational and Theoretical Nanoscience 5, 1-4
[7] Cleri F and Rosato V 1993 Phys. Rev. B 48, 22
[8] Michailov M 2009 Phys. Rev. B 80, 035425
[9] Landau D P and Binder K 2000 A Guide to Monte Carlo Simulations in Statistical Physics, Cambridge University Press, 2000
[10] Michailov M in: “Nanophenomena at Surfaces: Fundamentals of Exotic Condensed Matter Properties” 2011 Springer Series in Surface Science, Ed. M. Michailov, vol. 47, Chapter 6
[11] Giesen M and Ibach H 1999 Surf. Sci. 431, 109