Two-dimensional nanowires on homoepitaxial interfaces: Atomic-scale mechanism of breakdown and disintegration

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Abstract. We present a model for hole-mediated spontaneous breakdown of a homoepitaxial two-dimensional (2D) flat nanowire based exclusively on random, thermally-activated motion of atoms. The model suggests a consecutive three-step mechanism driving the rupture and complete disintegration of the nanowire on a crystalline surface. The breakdown scenario includes: (i) local narrowing of a part of the stripe to a monatomic chain, (ii) formation of a recoverable single vacancy or a 2D vacancy cluster that causes temporary nanowire rupture, (iii) formation of a non-recoverable 2D hole leading to permanent nanowire breakdown. These successive events in the temporal evolution of the nanowire morphology bring the nanowire stripe into an irreversible unstable state, leading to a dramatic change in its peculiar physical properties and conductivity. The atomistic simulations also reveal a strong increase of the nanowire lifetime with an enlargement of its width and open up a way for a fine atomic-scale control of the nanowire lifetime and structural, morphological and thermodynamic stability.

1. Introduction

Metal nanowires excite remarkable academic curiosity as physical systems with confined geometry, reduced dimensionality and peculiar quantum properties, [1-10]. They also hold special attention in contemporary nanoscale material science because of the large number of exotic technological applications. Being physical objects with reduced space dimensions, the atomic nanowires demonstrate a variety of extraordinary features related mostly to their electronic conductivity. In these systems, which are considered as the ultimate quantum conductors, the electrons are able to propagate freely, without scattering, which leads to a dramatic variation of the nanowire conductivity, respectively, the electrical resistance. This is why in the last decades the basic mechanisms of nanowire growth have been studied in great detail by considering the formation of one or more linear atomic chains via different methods, including scanning tunneling microscopy (STM) tip-based methods, break-junction techniques, and epitaxial growth on vicinal and atomically smooth crystal surfaces. These theoretical and experimental studies have been generally focused on the problem of how to create nanowires [1-4]. Considerably less attention has been paid to the thermodynamic stability, rupture and complete disintegration of these exotic structures [11-13]. For this reason, the present work deals with the opposite issue of how nanowires spontaneously breakdown as a result exclusively of the random motion of their building atoms.

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Recently we suggested a general atomic-scale scenario of a breakdown mechanism and complete disintegration of metal monatomic nanowires, freely standing in space or located on a crystalline substrate [11-13]. This research dealt with single atomic chains being exposed exclusively to the random thermal motions of their atoms without any impact of external fields (elastic strain, magnetic or electric forces, etc.). The specific linear atomic configuration of this ensemble of particles strongly deviates from that required for thermodynamic equilibrium and tends spontaneously to minimize its Gibbs free energy. Hence, at any finite non-zero temperature, the nanowire atomic configuration passes through a sequence of local energy states minima. This structural time evolution and atomic reorganization leads to a loss of continuous linear ordering of the nanowire via a multi-step mechanism of rupture at random sites and formation of small, differently sized clusters on the epitaxial interface. As a result, the ensemble of atoms finally loses its peculiar physical and electronic properties. This particular scenario of breakdown and complete disintegration quantifies the finite lifetime of the nanowire, which is intimately related to the nanowire conductivity as one of the most essential feature of this physical system.

In the present study, our previously suggested physical and computational model for single monatomic chains is extended to flat, two-dimensional (2D) monolayer thick nanowire with variable width, figure 2. These flat nanowires are constituted of finite atomic chains located on crystalline substrates of the same material. Being ordered parallel to each other and touching themselves, they form 2D atomic stripes. Here, we discuss the impact of the nanowire’s width and temperature on its structural stability affected by formation of atomic vacancies, vacancy clusters, step anisotropy, nanowire narrowing and generation of 2D wave-shaped atomic morphology. On that background we evaluate important physical quantities, such as the probability of breakdown, life time and the mechanism of complete disintegration. Since we focus our study on nanowires that are not exposed to any external fields, we exclude the impact of lattice mismatch between the nanowire and substrate. This is why in our model we use nanowires of the same material as that of the substrate. Hence, we consider the nanowire rupture and its disintegration as processes

**Figure 1.** Hole-mediated breakdown of a nanowire on a crystalline surface. The time evolution reveals a multi-step rupture mechanism leading to complete nanowire disintegration: (a) - initial configuration; (b) - formation of active sites (precursors); (c) - generation of single vacancy; (d) - generation of hole (double vacancy) and (e) - formation of 2D atomic clusters ([12], [13]).

**Figure 2.** Non-recoverable vacancy cluster (hole) and permanent breakdown of nanowires with variable width. Atomically smooth fcc(111) homoepitaxial interface at 500 K: (a) - monatomic nanowire; (b), (c), (d) - nanowire 2D stripe consisting of 2, 3 and 4 monatomic chains, respectively. Generation of 2D wave-shaped atomic morphology on the stripe is clearly seen.
activated only by thermal motion of atoms. Let us point out here that the misfit between nanowire and substrate could stabilize the linear atomic chain or, in contrast, could facilitate its rupture, depending on the value of the lattice mismatch and the anisotropy of the epitaxial interface. This analysis is a subject of a separate study.

2. Physical and computational models

The analysis of the nanowire stability, breakdown and complete disintegration is based on an atomistic simulation experiment within the framework of the physical and computational models outlined below. The physical model in the present study is designed to reveal the temporal, structural and morphological evolution of 2D flat atomic nanowires at a constant temperature $T$. These flat nanowires are constituted of several atomic chains located on a homoepitaxial interface. Being ordered in a parallel way in contact with each other, they form atomic configuration similar to stripes, figure 2. The interface on which the nanowires are placed is atomically smooth, step free Cu (111) crystal surface. Being bound via many-body interacting potential, all atoms of the system (substrate and nanowire) are exposed to random thermal fluctuations only. The computational model is grounded on classical atomistic Monte Carlo (MC) sampling, with many-body tight-binding second-moment approximation potential between the interacting atoms [14-16]. The statistical distribution in our model is canonical, i.e. an NVT ensemble with a constant number of particles, $N$, at a fixed temperature, $T$, and volume, $V$, [17, 18].

Following this approach, the total interaction energy $E_i$ of atom $i$ in the system is expressed by

$$E_i = E_i^r + E_i^b,$$  \hspace{1cm} (1)

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

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

Here, $r_0$ 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 (3 atomic distances in our model). The first term in equation (2) is a Born-Meyer ion-ion type 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 [14]. In equation (2), $\xi$ 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, $\xi$ 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-neighbors distance in the bulk crystal. The values of the hopping integral $\xi$ and all related parameters $A$, $p$, and $q$ in equation (2) are taken from [14,16]. In equilibrium, the system energy reaches its minimum and fluctuates around a constant value. Full lattice dynamics of all nanowire atoms ensures the complete relaxation of the system. All simulations are grounded on a three-dimensional continuous space model, i.e. substrate and 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 set of linear monatomic chains with...
periodic boundary conditions along the chains axis. All simulation data are averaged over 10 runs with the nanowire stripe at specific width and temperature. 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 100 Monte Carlo Steps (MCS). The generation of structural defects in the atomic stripe: single atomic vacancy, double vacancy, vacancy clusters, 2D atomic islands, etc. are detected during the simulations by measuring the distance between the atoms building the nanowire and via visual inspection of the snapshots taken on every run. 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, 13, 16].

3. Results and discussion
Before discussing the breakdown scenario of the flat 2D nanowire, let us point to an important detail related to the nanowire atomic morphology and anisotropy on an fcc(111) interface. The interface anisotropy leads to a different step free energy, relaxation ability, and diffusion barrier for displacement of the nanowire atoms in directions A and B, figure 3, [11, 12, 15]. This effect acts on the atomic step roughening transition, which is considered in our model as a precursor to the nanowire narrowing, breakdown and disintegration. Therefore, the breaking process is not symmetric in directions A and B and depends on the substrate surface orientation through the anisotropy of the surface atomic dynamics in different directions. Let us note that the temperature-dependent atomic roughening of B-steps costs less energy compared to that of A-steps. This is not the case at high temperatures, where this difference disappears since the thermal diffusion energy of atoms belonging to the steps is higher than the energy barrier for perpendicular translation in both directions, figure 3.

![Figure 3. Anisotropy of thermal fluctuations of nanowire atoms and resulting equilibrium atomic structure of A- and B-steps at 300 K and 400 K on an fcc(111) substrate. The initial atomic configurations of A- and B-steps are presented in the middle panel of the figure ([11]).](image)

The time evolution of the nanowire 2D stripe reveals a multi-step breakdown mechanism that could be considered as a sequence of well-defined structural changes and different morphological states. Let us note that our atomistic simulations are conducted at a constant temperature and the nanowire stripe build-up of variable number of monatomic chains follows a path toward its equilibrium atomic configuration. Our simulation results demonstrate that the nanowire narrowing at random places precedes the nanowire rupture. Hence, we observed that a nanowire breakdown starts preferentially from the step with a lower atomic roughening transition temperature. This is a result of the lower desorption energy for the atoms that belong to the atomically rough step and which facilitates the formation of locally concave areas on an initially linear ordering of the stripe. Since, however, the nanowire is wider than the monatomic chain, the formation of an entropy-driven wave-shaped structure is less favorable than that of the latter. In that case we consider the local nanowire narrowing as an active site for breakdown due to atomic roughening of the nanowire steps. The nanowire rupture occurs when the narrowing that has appeared randomly at one of the nanowire steps becomes greater than the nanowire width. This process is manifested in figures 4a-4d, which illustrate the time evolution of a nanowire having four monatomic chains.
Figure 4. 500 K. Temporal evolution of a nanowire constituted of 4 monatomic chains - multi-step breakdown mechanism:
(a) local concave thinning - 60 0000 MCS and (b) 120 000 MCS;
(c) - formation of a vacancy - 180 000 MCS;
(d) - formation of hole (vacancy cluster) permanent nanowire breakdown - 300 000 MCS.

The probability $P_v$ of appearance of at least one vacancy in the nanowire until time $t$, defined as $P_v(t) = N_v(t)/N_{tot}$ is one of the parameters that characterize the temporary nanowire rupture at a certain temperature. Here $N_v(t)$ is the number of nanowires possessing at least one vacancy until time $t$, and $N_{tot}$ is the total number of nanowires studied. Our results reveal that this probability dramatically decreases with enlargement of the nanowire stripe width, which is clearly seen in figure 6.

Figure 5. Recoverable vacancy formation and temporary breakdown of a nanowire constituted of 3 monatomic chains at 500 K:
(a) concave thinning – 26000 MCS;
(b) vacancy formation – 49000 MCS;
(c) vacancy recovering by randomly diffusing atom – 53000 MCS;
(d) vacancy formation on the same place – 57000 MCS;
(e) new recovering event – 73000 MCS.

Figure 6. Time dependence of the probability $P_v(t)$ to form at least one vacancy at 500 K for nanowire consisting of 1, 2 and 3 monatomic chains.

Figure 7. The average time (in MCS) for generation of single atomic vacancy, $\tau_v$, and non-recoverable vacancy cluster (hole), $\tau_H$, dependent on the nanowire width, at 500 K and 700 K.
The atomistic simulations reveal also that the enlargement of the nanowire stabilizes the linear chain structure and increases the lifetime. This is clearly seen in figure 7 where the average time for formation of vacancy and non-recoverable hole grow exponentially with increasing the nanowire width. As we have already pointed out, in the case of nanowire constituted of more than one monatomic chain, the breakdown probability will be complicated function of the probability for rupture of every individual monatomic chain that belongs to the nanowire. The evaluation of this probability is quite complex since two vacancies that are created in each monatomic chain have to be randomly generated very close to each other. This additional requirement is indispensable for generation of a non-recoverable atomic cluster that causes nanowire breakdown.

Similar to the case of monatomic nanowires is the formation observed by us of two types of atomic vacancies. The first type are recoverable vacancies, since they can be filled up back by the randomly walking atoms already detached from the nanowire in the vicinity of the single vacancy or vacancy cluster. This kind of vacancies cause only temporary breakdown of the integrity, and, hence of the conductivity, too, figure 5. Considerably more important and physically significant is the second type of vacancies, representing a vacancy cluster leading to permanent nanowire rupture. At a given size of this cluster, which we consider as a non-recoverable hole, the probability of its being filled up by randomly diffusing atoms is practically zero, figure 4. Therefore, the n-chain atomic nanowire follows three-step mechanism of breakdown and complete disintegration, as follows: (i) concave narrowing at a random location on the nanowire, figure 4b; (ii) generation of a single atomic recoverable vacancy, figure 4c; and (iii) formation of a non-recoverable vacancy cluster, figure 4d. Then this process can be schematized as:

\[
\begin{align*}
S \xrightarrow{\omega_v} C \xrightarrow{\omega_{hv}} V \xrightarrow{\omega_{sh}} H
\end{align*}
\]

Here S, C, V and H stand for a straight morphology state (S), a concave morphology state (C), a vacancy state (V), and a hole state (H), and \(\omega_{hv}, \omega_{sh}, \omega_{vh}, \omega_{hv}, \omega_{cv}, \omega_{hv}\) are the corresponding frequencies of S-C, C-V, V-H, H-V, V-C and C-S transitions. This description accounts for the real dynamics of generation and annihilation of different structural and morphological defects and is essential in the kinetic treatment of nanowires breakdown.

It is important to compare the single-vacancy formation in a monatomic nanowire, figure 1, and a nanowire stripe comprising two, three, four, etc. single atomic chains, figure 2, [12,13]. The first difference is presented in figure 4. The probability of generation of two, three or more vacancies (depending on the nanowire stripe width) at the same time and place and, thus, of creation of a single atomic vacancy in the whole nanowire is very low. This probability is a function of the individual probabilities of single-vacancy formation in each monatomic chain that builds up the stripe. Moreover, these vacancies have to be generated very close to each other or at the same place in the nanowire. This is why, a flat 2D nanowire breaks down via the mechanism of narrowing at certain places, instead of waiting for the simultaneous random generation of single vacancies at this place at the same time. Apparently, this process of stripe narrowing is energetically more favorable and hence more probable than the simultaneous generation of individual vacancies at the same location. Let us point out that once a single atomic vacancy is generated at one of the atomic step (A or B) of the stripe, the enlargement and development of this vacancy into a vacancy cluster is favored compared to the flat atomic step. This is because the generation of kinks on the step and detachment of the atoms from these kink positions costs less energy than a detachment from the flat, atomically smooth step. Moreover, detachment of atoms from the kinks does not change the line step energy. Therefore, the generation even of a single atomic vacancy at a given step (A or B) favors the process of narrowing the nanowire by formation of a locally concave shape morphology in the stripe.

The second difference relates to the critical size of the vacancy cluster. Our results clearly demonstrate that the cluster size for non-recoverable breakdown is larger than that of the single monatomic nanowire (two neighboring vacancies). This critical size depends on the nanowire width.
Being with a larger width because of the several monatomic chains in it, the 2D nanowire has more atoms that can participate in the random fill up of the single vacancy or the vacancy cluster. The atomistic simulations reveal that at a fixed vacancy cluster size, the number of recoverable events in the temporal evolution of the flat 2D nanowire increases with the nanowire width, figure 6. Therefore, widening the stripe width increases the critical size of non-recoverable cluster. It should be pointed out also that the recovering mechanism kinetics is tightly dependent on the mean free diffusion path of atoms, respectively, on the interface temperature.

We can also define the quantity mean lifetime of recoverable vacancy and vacancy cluster. These quantities reveal for how long a nanowire will be in a state of temporary loss of conductivity before being recovered. Our qualitative evaluation shows that this lifetime decreases with the enlargement of the nanowire width. This indicates that at a fixed temperature the wider nanowires will recover more easily compared to the monatomic nanowires. This effect is due to the larger number of atoms taking part in random diffusion in the vicinity of the recoverable vacancy and vacancy cluster. If the distance between the newly created ends of the nanowire as a result of vacancy formation is equal to one atomic distance, figure 5b and figure 5c, then only one randomly walking atom could fill up the vacancy between these ends.

4. Conclusions
The present study provides insight into the mechanism of random thermal rupture of 2D flat homoepitaxial nanowire constituted of two, three or more atomic rows and located on an atomically smooth fcc(111) interface. The structural and morphological temporal evolutions of the nanowire reveal three consecutive steps of rupture, as follows: (i) local narrowing of a part of the stripe up to a monatomic chain, (ii) formation of a recoverable single vacancy or a vacancy cluster that cause temporary nanowire rupture, and (iii) formation of a non-recoverable hole leading to permanent nanowire breakdown. Analyzing these successive events in the temporal evolution of the nanowire morphology, we observe that the nanowire narrowing causes formation of randomly distributed locally concave areas in the nanowire, which could generate inhomogeneity in the nanowire conductivity, figures 4b, 5c and 5e. The increase of the stripe width leads to a significant enhancement of the nanowire lifetime. In contrast to a single monatomic nanowire, temporary rupture takes place not only upon single atomic vacancy generation, but also upon the generation of a vacancy cluster that can be also recoverable. This is an essential difference with the case of a monatomic nanowire, where only a single atomic vacancy can be recovered. The lifetime of the recoverable cluster is considerably smaller compared to that of the monatomic nanowire. The size of a non-recoverable hole depends on the nanowire width and increases with its enlargement. Experimental research in this direction could significantly contribute to a better understanding of the methods for atomic-scale control of the nanowire stability, lifetime and rupture kinetics.

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