

Instability of an atomic chain arising from lattice misfit

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We have used molecular-dynamics to exemplify the instability and structural dynamics of an atom chain on a crystalline substrate with a lattice misfit between the chain and substrate. To clarify the key issues without any unnecessary complications, we chose the anisotropic Au(110)-(1×2) reconstructed surface as the substrate to host a surface atom chain, and compared the properties of Ni and Au chains, which, respectively, represent chains with and without lattice misfit. For Ni/Au, we found that a chain of five Ni atoms matches the linear dimension of four Au atoms along the Au $\langle 1\bar{1}0 \rangle$ direction, and the central Ni atom forms a dislocation. The chain stability fluctuates as more atoms are added to the chain because additional dislocations are formed. Chain breakage and initiation of two-dimensional growth also always start at dislocation centers. In comparison, for Au/Au, which has no lattice misfit, a chain grows smoothly and always dissociates by releasing an atom from either end of the chain.

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I. INTRODUCTION

Research on quasi-one-dimensional systems such as adsorbed atom chains has drawn much attention because these systems often display rather unusual physical, chemical, and mechanical properties. The simplicity of these atom chains, on the other hand, enables thorough theoretical studies of them, for the development of new physical models describing the fundamental physics and chemistry of these nanostructures. Among all attributes affecting the practical applicability of a novel nanostructure, structural stability perhaps is the most important one. Studies of structural stability concern issues including diffusion mechanisms of atoms on the host surface of the nanostructure, the nucleation and growth of an atom cluster, the structural configuration of the cluster, the release and recapturing of constituent atoms, and concerted motion of the cluster.

Experimental imaging of surface atoms and their motions on a crystalline substrate by field ion microscopy¹⁻⁴ and scanning tunneling microscopy^{5,6} have unambiguously revealed various diffusion mechanisms of adatoms, the alignment of adatoms in an atom chain configuration, and the structural dynamics of such an atom chain. In addition, a series of theoretical studies of relevant energy barriers and molecular-dynamics simulation have been conducted and largely deepened our understanding of these experimental results. Many of these studies have chosen the missing-row trough on a reconstructed fcc-(110)-(1×2) surface as a model system, because the trough is a perfect one-dimensional template to study atom diffusion along the trough and the structural stability of an atom chain in the trough. For the former case, one would intuitively assume a simple one-dimensional atom diffusion at the bottom of the

trough. But both experimental results and theoretical calculations have shown that such an intuition can be erroneous.^{7,8} For example, we now know that both for a gold atom at the bottom of a trough of Au(110)-(1×2),⁷ and a platinum atom on Pt(110)-(1×2),⁸ atom diffusion does not only proceed by moving at the bottom of the trough (direct jump) but also by climbing up and walking on the sidewall facet of the trough. In fact, the diffusion energy barrier for direct jump is not necessarily less than that of facet metastable walk.⁸

The movements, structural stability, and structural dynamics of atom clusters in a fcc-(110)-(1×2) trough are even more intriguing than atom motions. Starting from the simplest picture of a dimer, we now know that a “concerted jump” of the dimer, i.e., the atom pair moves together, is normally not the most favorable motion. For both Au₂/Au(110)-(1×2) (Refs. 9 and 10) and Pt₂/Pt(110)-(1×2) (Refs. 10 and 11), dimer diffusion mainly proceeds via a leapfrog mechanism in which one atom climbs up the sidewall of the trough, makes a jump, and subsequently falls back to the channel bottom beside the stationary atom of the original dimer. Another less favorable motion mechanism involves a sequence of dimer dissociation, atom diffusion, and recombination of two atoms into a dimer. For example, the semiempirical theoretical studies showed that for Au₂/Au(110)-(1×2), the respective energy barriers for leapfrog, concerted jump, and dissociation-recombination are 0.45, 0.51, and 0.52 eV.⁹

The above examples concern self-diffusion in homoepitaxial systems such as Au atoms on a Au crystal and Pt atoms on a Pt crystal. When we put foreign atoms on a crystal surface, different combinations of chemical bonds are expected to influence the structural stability and structural dynamics. A thorough explanation of such a picture has not yet

been drawn, although fragments of relevant data have already emerged. For example, we found recently that Ni dimers in the trough of Au(110)-(1×2) are more agile than Au dimers.¹² In comparison, Montalenti and Ferrando⁹ found that the respective theoretical energy barriers for leapfrog, concerted jump, and dissociation-recombination for Cu₂/Au(110)-(1×2) are 0.75, 0.66, and 0.50 eV. Hence, a Cu dimer in the trough of Au(110)-(1×2) is less mobile than an Au dimer. Furthermore, a Cu dimer tends to diffuse via dissociation-recombination instead of leapfrog. Montalenti and Ferrando⁹ speculated that the different stability between a Cu dimer and Au dimer is probably related to a size-mismatch effect. We believe that their recognition of the importance of size mismatch is insightful, and further studies in this direction are justified.

With this theme in mind, we found in the literature further hints about the effects of misfit in a quasi-one-dimensional system. For example, for an atom chain on a crystalline surface, dependence of chain stability on chain lengths has been independently found in systems such as Ir and Pd on W.^{1,2,13} We believe that this dependence is consistent with the “magic size effects” of the stability of hypothetical two-dimensional (2D) heteroepitaxial islands on a crystal surface revealed by Hamilton.¹⁴ Hamilton explained this size dependence by lattice misfit between the island and substrate. In addition to these studies, the earlier molecular-dynamics simulations by Luedtke and Landman are also relevant.¹⁵ They compared the collapse of a two-layer cluster of Au on Au(111) to that of Au on Ni (100) and found that the latter is easier than the former because of interfacial misfit between Au and Ni.

The studies of chain stability have recently been extended to include the analysis of diffusion mechanisms of atom chains. For example, Au and Pt chains were studied by Montalenti and Ferrando,¹⁶ Pt, Au, Cu, and Ni chains by Kürpick, Au_n/Au(110)-(1×2) and Pt_n/Pt(110)-(1×2).¹⁷ Logically, examination of the effects of misfit will further unveil interesting diffusion mechanisms, which are not found in homoepitaxial systems such as those in the above examples.

In this work, we report on a comparison of the behaviors of Ni chains and Au chains in a trough of Au(110)-(1×2), to illustrate how lattice misfit can change structural stability of the chain as a function of chain length. Furthermore, we used molecular dynamics to illustrate the effects of lattice misfit on possible structural changes and diffusion mechanisms of the Ni chains.

II. DETAILS OF CALCULATIONS

We used the Johnson alloy potential,^{18,19} which was deduced from the embedded-atom methods,^{20,21} to describe atomic interactions for Ni and Au. To test the validity of the potential in describing the surface properties of a gold surface, we performed molecular-dynamics simulations of the properties of the Au(110)-(1×2) surface. The results show that the surface is stable until 600 K, in agreement with the experimental data in the literature.²² We have also calculated the properties of isolated Ni_n clusters by using the Johnson potential. The obtained ground-state structures are very close

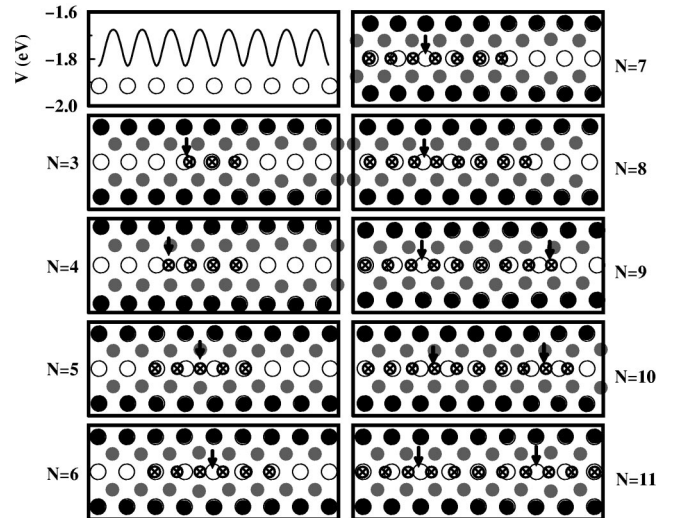


FIG. 1. The energy of a single Ni atom on the trough of Au(110)-(1×2) as a function of its position, and the equilibrium structures of Ni atom chains on Au(110)-(1×2) for 3–11 Ni atoms. The open circles denote Au atoms at the bottom of the trough, the filled black dots denote Au atoms at the top row of the trough, the circles with crosses are the Ni atom. The arrow decorates a dislocation.

to the results predicted by the Fermi-surface potential^{23,24} and other known *ab initio* results.²⁵ This alloy potential has also been successfully used previously by us to simulate the diffusion of Ni clusters on the Au(110) missing-row surface.²⁶ From these calculations, we conclude that the Johnson potential can properly describe the behaviors of Ni chains on Au(110)-(1×2).

In this work, the simulation cell consisted of 11 layers of Au atoms. Each layer contained 320 atoms, except for the topmost layer, which contained only 160 atoms due to the missing row. The atoms in the two bottom layers of the cell were kept static to mimic the underlying infinite solid. Periodic boundary conditions were imposed in the lateral direction to mimic an infinite surface. The simulation temperature, controlled by scaling the velocities of atoms in the two layers just above the static layers,¹⁵ was well below the temperature of the surface roughening transition, which is known to occur at about 650 K. This ensured that the surface structure remained stable during the simulation.

III. RESULTS AND DISCUSSIONS

A. Equilibrium structure of atomic chain

The potential energy V for a single adatom at the bottom of the trough as a function of its location, as shown in the top panel of Fig. 1, clearly indicates that the adatoms in the trough tend to sit on the top of the substrate Au atoms, to maximize the interaction with the substrate Au surface.

To get an approximation of the equilibrium structure of the chain in the trough, we optimized the structure of the atom chain by the standard steepest-descent method with more than ten initial configurations. For each initial structure, the chain atoms were randomly distributed along the

trough direction. The obtained results are summarized in Fig. 1, which shows the spatial relationship between Ni atoms in Ni_n chains ($n=3-11$) and the host Au atoms along the $\langle 1\bar{1}0 \rangle$ direction. The first thing to note is that the interatomic distance of Ni-Ni is shorter than that of Au-Au. More specifically, our calculation shows that the interatomic distance in the isolated Ni chain structure is 2.23 Å. This is about 10% shorter than the nearest-neighbor distance in a Ni crystal (2.49 Å), which can be attributed to the decrease of the coordinations of an atom in the one-dimensional chain. The exact interatomic distance varies slightly as a function of chain length when the chain is placed on the Au surface because of the interaction between the atoms on the chain and the substrate. Still, the interatomic distance of Au-Au in the $\langle 1\bar{1}0 \rangle$ direction, 2.86 Å, is very different from the Ni-Ni distance in the chain. Indeed, for a chain of $n=3$, only the middle Ni atom sits on top of an Au atom with an optimal interaction between the Ni atom and the substrate, and the other two Ni atoms bond only weakly to the substrate. When the chain length increases to $n=5$, the middle Ni atom sits between two Au lattice points, and thus can be considered as a dislocation, a concept that was also used in the hypothetical heteroepitaxial model system of Hamilton.¹⁴ If we adjust the placement of the chain on the substrate such that the dislocation is not symmetrically situated in the chain, the energy increases. As n increases to 6, the dislocation remains near the middle of the chain and can now be described as one Au lattice point between two Ni lattice points. When n reaches 9, a second dislocation emerges near the end of the chain. For $n=11$, two dislocations can be seen in the chain. By comparing the chain structures of $n=6$ and $n=11$, we deduce that one dislocation can be found in every chain segment of $4a_0$, where a_0 is the lattice period of the Au(110) missing row surface along the $\langle 1\bar{1}0 \rangle$ direction.

To analyze the stability of $Ni_n/Au(110)-(1\times 2)$ as a function of chain length, we calculated the first-order energy difference, which is defined as $\delta E = E(n) - E(n-1)$. The data are summarized in Fig. 2(a), and those for $Au_n/Au(110)-(1\times 2)$ are also included as a reference. Clearly, for Au/Au where there is no lattice misfit and no dislocation formation, δE nearly remains constant for $n > 3$, which suggests that the structural stability of the Au chain on the Au surface is essentially independent of the length of the chain.

But for $Ni_n/Au(110)-(1\times 2)$, δE fluctuates with increase of chain size. From $n=4$ to $n=5$ and from $n=8$ to $n=9$, there are large decreases in δE , which represent the formation of dislocations in the center of the chain and on one end of the chain, respectively. The data in Fig. 2(a) also show that the chains of $n=4, 5, 9, 10$ all possess very low stability because of smaller values of δE . With these data, we conclude that the growth of Ni chains along $\langle 1\bar{1}0 \rangle$ of Au (110) at low temperature would favor the formation of chain segments with $n=6-8$.

B. Thermal dynamics

To further examine the structural dynamics of Ni/Au, we conducted molecular-dynamics simulations as a function of

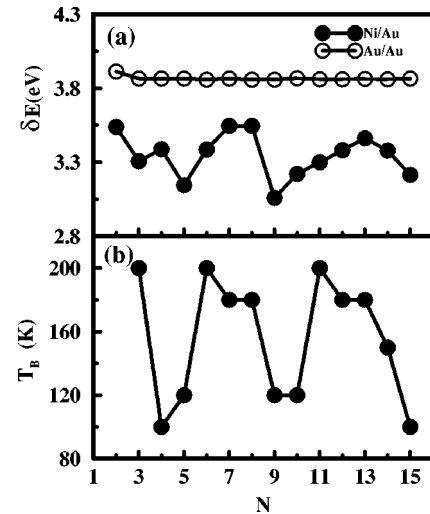


FIG. 2. Stability of the atom chain on the Au(110)-(1×2) surface. (a) The energy required to take an atom from an n -atom chain. (b) The threshold temperature T_B at which the atom chain dissociates.

growth temperature. At each temperature point, simulations were performed for about 20 000 steps with a time step of 8 fs. The simulation results show that the structure of a chain with a certain length can only be maintained up to a certain temperature above which the chain breaks, with atoms leaving the chain and transforming the chain into a two-dimensional structure. The data on such threshold chain-dissociation temperature as a function of chain length are shown in Fig. 2(b). The simulations indicate that once the chains such as Ni_3 , Ni_6 , Ni_7 , Ni_8 , and Ni_{11} are formed, they are stable up to about 200 K. In comparison, the chains such as Ni_4 , Ni_5 , Ni_9 , and Ni_{10} are relatively easy to break. These results are consistent with the energy data shown in Fig. 2(a). In the present work, the energy data in Fig. 2(a) and dissociation temperature data in Fig. 2(b) were calculated to illustrate a general trend in chain stability. We hope that this analysis will stimulate more accurate studies of structural energies, reaction energy barriers, and reaction kinetics.

A key issue in chain stability is how a one-dimensional structure breaks and transforms into a two-dimensional structure. The molecular-dynamics snapshots which capture the process when a Ni_5 chain breaks at 120 K are shown in Fig. 3(a). The instability of the chain first appears near the core of the dislocation at atom c , which is reasonable because atom c is not directly bonded to any Au atoms. As soon as atom c jumps off the chain, a nearby atom, atom b , in the chain moves to the vacancy left by atom c . After a sequence of atom motions, a 2D structure with an atom attaching to the side of a four-atom chain is formed (structure II in Fig. 3). Since atom c , after jumping off the chain, is near the metastable position on the sidewall of the trough, our molecular-dynamics data also show that atom c moves easily along the side of the four-atom chain but it never comes down the chain again, at least not within our simulation time limit. In fact, our static energy calculation shows that atom c needs to overcome a barrier of 0.68 eV before it can join the chain again.

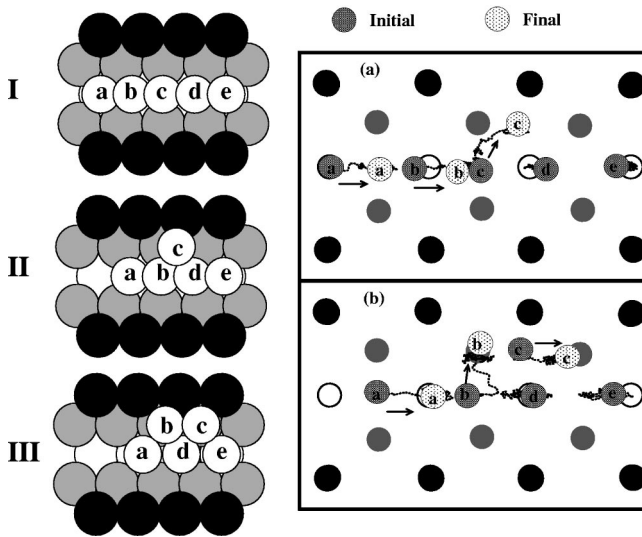


FIG. 3. The dynamical process of Ni_5 changing from a one-dimensional chain to a two-dimensional cluster at 120 K. The chain dissociation first occurs near the dislocation.

An example of further dissociation of structure II is shown in Fig. 3(b). In the dissociation process, the four-atom chain of structure II in Fig. 3 breaks and releases atom b to join atom c . Not unlike the dissociation of the five-atom chain of structure I, the breakage of the four-atom chain does not happen by releasing an atom from one of the two ends of the chain. In fact, the intuition that predicts chain shrinkage by releasing an atom from one of the two ends of a chain only works for the Au/Au system where there is no lattice misfit. The molecular-dynamics snapshots of such a chain shrinkage process are shown in Fig. 4. Like the Ni/Au structure II in Fig. 3, once an Au atom is moved up to the side of an Au chain, the Au atom moves back and forth easily. If the moving atom originates from one end of the chain, moves towards the other end of the chain, and drops back to the chain, the overall motion can be perceived as if the chain has slipped. This chain motion has indeed been observed experimentally for a Pt chain on the Pt(110)- (1×2) surface.²⁷ Similar motions of an Au chain on the Au(110)- (1×2) surface have also been shown by molecular dynamics.¹⁰

Finally, we have also repeated the same molecular-dynamics calculations to other Ni/Au chains and found chain-dissociation processes similar to those in Fig. 3. Typically, chain dissociation is initiated by releasing an atom from the center of a dislocation. For long chains, the double-row structures (structure III) in Fig. 3 are stable to about 250 K above which more compact islands are formed. This is consistent with the experimental data of Hugenschmidt

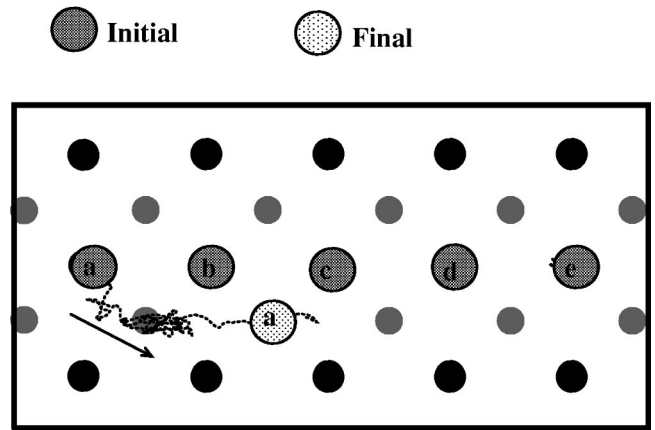


FIG. 4. The instability of an Au chain. The instability starts from one of the two ends of the chain.

et al.,²⁸ which revealed that the double-row structure of Ni on Au(110)- (1×2) are predominate at 220 K but 2D islands are present at 300 K. From our simulation results, we further infer that the diffusion of long Ni atom chains at an elevated temperature likely proceeds through a 1D-2D transformation, together with the dynamics of atoms at dislocation sites, leaving their equilibrium positions and the peripheral atoms readjusting their positions.

IV. CONCLUSION

In summary, we have studied the structure, stability, and structural dynamics of Ni and Au atomic chains on Au(110)- (1×2) by using the molecular-dynamics method. We found that dislocations periodically appear in a long Ni chain, due to the lattice misfit between the Ni chain and Au substrate. The atoms at and near the dislocation sites are the chain constituents most likely to leave the chain. The misfit also leads to a size-dependent chain stability, which favors the formation of short chains with a certain size at a certain temperature. From dynamical simulations of chain dissociation and 1D/2D transformation, we found that the presence of misfit and thereby dislocations in a heteroepitaxial chain can alter the chain mobility mechanisms significantly from those of a homoepitaxial chain.

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