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Dynamic Ad-Dimer Twisting Assisted Nanowire Self-Assembly on Si(001)

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Based on *ab initio* total energy calculation, we show that a dynamic ad-dimer twisting assisted (DATA) process plays a crucial role in facilitating a novel structural reconstruction involving surface and subsurface atoms on Si(001). It leads to self-assembly of long nanowires of group-V elements (Bi, Sb) in the trenches of surface dimer vacancy lines (DVLs) with a characteristic double-dimer configuration. The key to this is the lowering of the kinetic barrier by the DATA process in conjunction with a favorable interaction between ad-dimers and step edges in DVLs. The present results provide an excellent account for experimental observations and reveal the atomistic origin and the dynamic transformation path for nanowire self-assembly on Si(001).

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The fabrication of nanostructures such as quantum dots and nanowires on semiconductor surfaces is at the heart of the next generation of electronic devices. Surface defects such as steps, kinks, and vacancies play important roles in thin film growth processes. Well defined surfaces provide a good template for the self-assembly of nanostructures, which holds the key to successful device applications. One approach to grow nanowires is to use preexisting steps as templates and deposit Ge and Si alternately in the step-flow growth mode [1]. Another approach is to use the strain energy of a lattice mismatched epitaxial layer. This technique has the advantages of low cost and high throughput. It has recently been used to grow Bi nanowires on Si(001) through a self-assembly process [2–5]. The width of a Bi nanowire is just 4 times the lattice constant of the Si(001) surface, ~ 1.5 nm, but the length can be as long as 40 ~ 200 nm. The direction of Bi nanowires is perpendicular to the surface Si-dimer rows. Each Bi nanowire consists of two adjoining chains of Bi dimers with the direction of Bi dimerization parallel to the chain. A last STM analysis of the surface condition before and after the Bi deposition shows that Bi nanowires are formed in the trenches of the vacancy line defects that stretch in the [011] direction on the terrace [5]. Similar nanowire structures have been observed for another group-V element Sb adsorbed on a hydrogen-terminated Si(001) surface [6] and for the 4*f* element Er on Si(001) [7]. It thus appears that the self-assembly of long nanowires with a double-dimer line configuration is a common phenomena on the Si(001) surface.

A double-core odd-membered ring (referred to as 5-7-5 hereafter) structure at Si(001) was recently proposed [4] for Bi/Si(001) nanowires [a quite similar 5-7-5 structure at As/Ge(001) step edges was also reported in Ref. [8]]. It is found that the 5-7-5 structure is an energetic advantage over other candidate models by Bowler and Owen using tight-binding and first-principles calculations [9]. We also

discussed the structural stability by the *ab initio* technique [10]. However, there is still a lack of understanding for the atomistic mechanism and the dynamic transformation path that leads to the self-organization of the proposed structural model. Moreover, the role of the surface dimer vacancy lines in the growth process and the origin for the characteristic double-dimer configuration of the nanowire remain unresolved.

In this Letter, we examine both the energetics and the kinetics of the group-V adatoms (Bi, Sb, As) on Si(001) under the *ab initio* total energy calculation. We show that a dynamic ad-dimer twisting assisted (DATA) process plays a crucial role in inducing a novel structural reconstruction involving surface and subsurface atoms on Si(001). It leads to the self-assembly of long nanowires of Bi and Sb with a double-dimer line configuration. Meanwhile, the difference in atomic size mismatch and chemical reactions prevent the formation of As nanowire on Si(001).

The reported *ab initio* total energy calculations are carried out using the Vienna *ab initio* simulation package (VASP) code [11], employing a plane wave basis set with a 200 eV cutoff energy and the generalized gradient approximation [12]. The electron-ion interaction is described by ultrasoft pseudopotentials [13]. The supercell size is set to $XYZ = 7.68 \text{ \AA} \times 30.72 \text{ \AA} \times 35.72 \text{ \AA}$ with ten layers of silicon, one layer of hydrogen to passivate the lowest Si layer, and a vacuum layer of about 20 \AA in the Z direction. In all calculations, the top seven layers are fully relaxed while the bottom three are fixed at the bulk structure. The XY plane corresponds to a 2×8 slab with periodic boundary conditions. Forces on the ions are calculated through the Hellmann-Feynman theorem allowing a geometry optimization. The energy minimization is done over the atomic and electronic degrees of freedom using the conjugate gradient iterative technique with four *k* points in the X direction of the Brillouin zone.

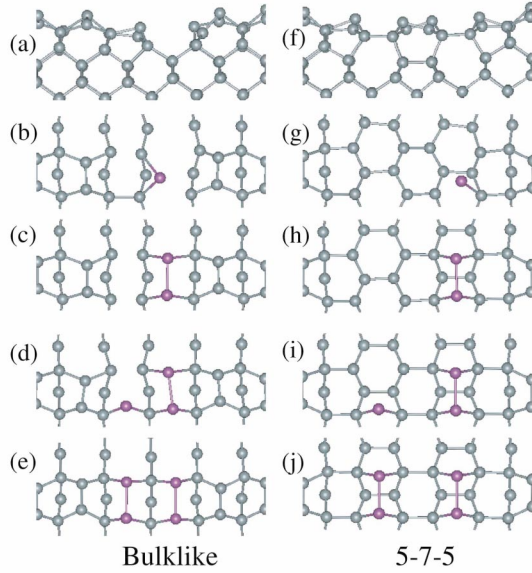


FIG. 1 (color). Stable configurations for zero to four group-V adatoms (purple balls) on Si(001) with bulklike and odd-membered ring 5-7-5 structures.

It is well known that missing dimer vacancies are always present on the Si(001) surface. They tend to elongate for *hundreds of nm* perpendicular to surface dimer rows, mostly forming two-dimer wide vacancy lines (2DVLs) at low surface vacancy densities [14–17]. Meanwhile, group-V surfactants (Bi, Sb, As) favor a layer-by-layer growth mode on Si(001) with reduced surface free energy. Arriving atoms float on the grown film, change the surface structure, and influence the kinetics of the deposited atoms. In this work we use the dominant 2DVL configuration to represent the vacancy lines on Si(001). The migration of group-V adatoms on Si(001) is relatively easy [18]. However, they become trapped in the 2DVLs through the interaction with the step edges (see below). Consequently, nanowires stretch along trenches of 2DVLs on the terrace as observed in experiment [5].

TABLE I. Calculated adsorption energy (E_{ad} , in eV/atom) for Bi, Sb, and As adatoms on Si(001) with bulklike [Figs. 1(b)–1(e)] and 5-7-5 [Figs. 1(g)–1(j)] structures. Also listed are the adsorption energy for the ad-dimer, the (2×8) and (2×1) structures, and the migration barrier (E_B , in eV/dimer).

Structure	Bi	Sb	As
Figure 1(b)	−4.32	−4.32	−4.85
Figure 1(c)	−5.04	−5.31	−5.73
Figure 1(d)	−4.60	−4.93	−5.56
Figure 1(e)	−4.83	−5.22	−5.90
Figure 1(g)	−3.96	−3.93	−4.32
Figure 1(h)	−4.78	−5.05	−5.49
Figure 1(i)	−4.73	−4.98	−5.39
Figure 1(j)	−5.11	−5.38	−5.80
Ad-dimer	−4.65	−4.89	−5.38
(2×8)	−4.89	−5.25	−5.76
(2×1)	−4.72	−5.17	−5.87
E_B [Fig. 1(e) \rightarrow Fig. 1(j)]	1.13	1.19	1.31
E_B [Fig. 1(e) \leftarrow Fig. 1(j)]	1.68	1.53	1.12

We first search for stable configurations of Bi, Sb, and As adatoms buried in the trenches of the 2DVLs on Si(001). Figure 1 shows stable structures for zero to four group-V adatoms with bulklike and 5-7-5 configuration. Adsorption energies listed in Table I are defined as

$$E_{ad}[n] = (E[n] - E_0)/n, \quad (1)$$

where $E[n]$ is the total energy with n Bi (or Sb, As) atoms on Si(001), and E_0 is the total energy of the substrate with the most stable asymmetric 2DVLs shown in Fig. 1(a) [19]. Among the bulklike structures, the most stable configuration is 1(c) for Bi and Sb, and 1(e) for As, the next most stable configuration is 1(e) for Bi and Sb, and 1(c) for As. Among the structures with 5-7-5 rings, the most stable configuration is 1(j), and the next most stable configuration is 1(h) for Bi, Sb, and As. These results clearly show that Bi, Sb, and As adatoms tend to form dimers at the step edge, suggesting that their interaction with the step edge is energetically favorable. This explains the trend of group-V

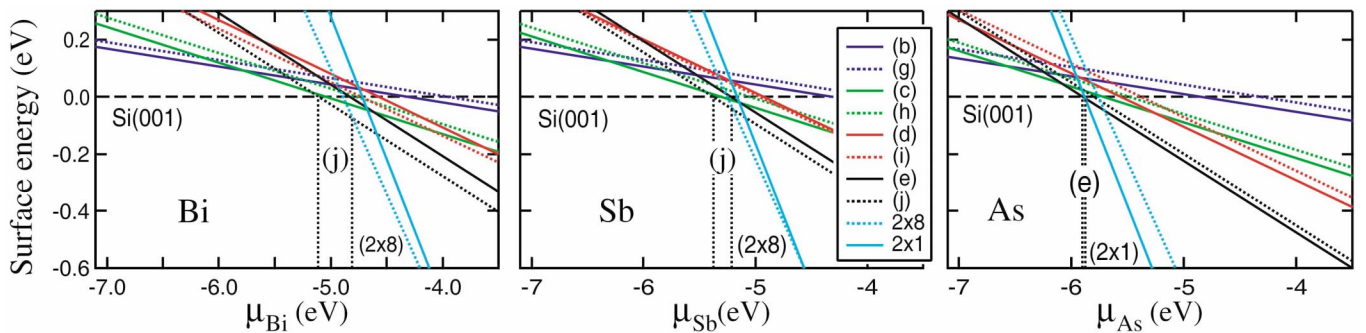


FIG. 2 (color). Relative surface energy as a function of the adatom chemical potential. Vertical lines divide different phase regions. Symbols of lines correspond to labels in Fig. 1. The corresponding bulk chemical potentials are -3.90 , -4.15 , and -4.70 eV per atom for Bi, Sb, and As, respectively.

surfactant nanowire formation in the trenches of 2DVLs. The metastable 5-7-5 structure has been observed on the As-terminated Ge(001) surface [8], and on the Sb/Ge(113) surface [20]. It is made possible by the low surface energy and the strain relief.

To assess the thermodynamic feasibility of the above scenarios, we have calculated relative surface energy $(E_{\text{ad}} - \mu_{\text{ad}})\theta_{\text{ad}}$ as a function of the chemical potential, μ_{ad} , and plotted it in Fig. 2. Here, the substrate chemical potential is already included in the definition of E_{ad} taken from Table I, and θ_{ad} is the adatom coverage. As the chemical potential of Bi (or Sb) increases, the surface structure changes from the Si(001) clean surface with 2DVL to the 5-7-5 structure 1(j) and then to the (2×8) structure at high Bi (or Sb) coverage. The 5-7-5 structure 1(j) is absent for As/Si due to the difference in atomic size mismatch and the reactions between As and Si. Two compounds, AsSi and As₂Si, exist in the equilibrium phase diagram [21], while no counterpart exists in Sb-Si and Bi-Si cases. In order to make the formation of the 5-7-5 structures 1(j) thermodynamically possible, it is found that the sources of the adatoms have deeper chemical potentials than the bulk chemical potentials based on the present calculations. It is worth noting that the structures with separated 1, 2, and 3 adatom configurations shown in Fig. 1 have not been observed for any of the group-V surfactants. This is consistent with the energetic preference for the double-dimer configuration shown in Table I. These

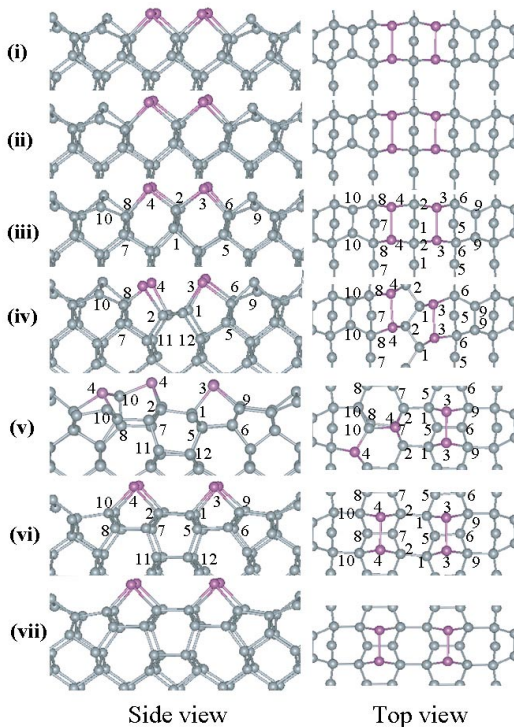


FIG. 3 (color). Top and side views of the atomic configurations along the transformation pathway.

results demonstrate that the formation of the 5-7-5 structure on Si(001) is favored at low coverage of Bi and Sb, in full agreement with experiment [5].

We now consider the underlying dynamic process for the nanowire formation. We have examined some possible transformation pathways, including various bonding configurations, identified the energetically most favorable one, and revealed the key role played by the DATA process in facilitating the transformation. Figure 3 shows the structural configurations along this proposed pathway. At each step, we fix the z ([001]) coordinates of the subsurface atoms labeled “1” that move up in steps, but allow full relaxation of their x and y coordinates. All other atoms in the top seven layers are also fully relaxed. We calculate the total energy and obtain structures at each step. From steps (i) to (iii), as the atoms 1 move up, atoms 2, 3, and 4 also move up slightly. About step (iv) atoms 1 and 2 start to rotate, and the two adjoining parallel dimers undergo a shear type shift relative to each other along the linear chain. The upward movement of atoms 1 and their rotation creates a strain field that yields reorganization of local bonding. Between steps (iv) and (v), one of the ad-dimers twists away from its linear chain position in coordination with the rotation of atom pairs 5-6 and 7-8 in the 2nd and 3rd layers. It is accompanied by a dynamic (transient) breaking of the ad-dimer bond. Finally, the deviated ad-dimer completes the dynamic twisting and returns to its original configuration, which restores the ordered linear chain with the reconstructed underlying 5-7-5 structure. In this process, the 5-7-5 structure first appears around step (iv) with the rotation of atoms 1 and 2 in the 2nd and 3rd layers, and then the double core appears with the rotations of atom pairs 5-6 and 7-8 in the 2nd and 3rd layers together with the rebonding between atoms 11 and 12 in the 4th layer. At the same time, four Si atoms 9 and 10 descend into the second layer from the top layer.

To illustrate the key role of the DATA process in the nanowire self-assembly on Si(001), we plot in Fig. 4 the relative total energy along the transformation pathway with fine steps around step (v). Without the DATA process, the energy keeps increasing from step (i) to (v) and *beyond* due to the compressive strain around the seven membered ring core and the bond breaking between atoms 1–12. However,

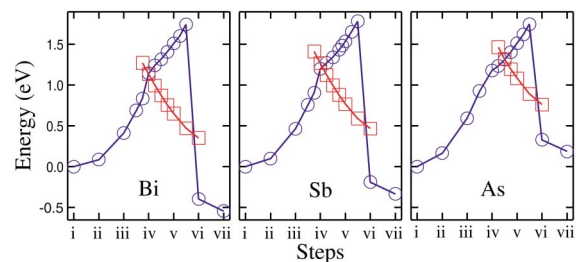


FIG. 4 (color). The relative total energy variation in terms of the steps taken along the pathway with (squares) and without (circles) the DATA process.

the DATA process reduces the energy around step (v) because of the stress release associated with the rotations of atoms 5-6 and 7-8 in the 2nd and 3rd layers and the rebonding between atoms 11-12 in the 4th layer as shown in Fig. 3. There is no Si bond breaking along the pathway. With the DATA process, the energy barriers are estimated to be 1.13, 1.19, and 1.31 eV/dimer for Bi, Sb, and As on Si(001), respectively. The barriers for Bi and Sb are similar because of their similar atomic sizes, whereas for As the difference is larger. It is interesting to compare these calculated barriers with existing data for similar systems and processes [18,22,23]. For example, the barrier for a Si ad-dimer diffusing along the dimer rows on a flat surface is 1.02–1.09 eV/dimer [22], and the energy barrier for single dimer vacancy diffusion along the dimer rows is 1.18 eV [23]. Moreover, considering the energy difference between the bulklike [step (i)] and 5-7-5 [step (vii)] structures shown in Fig. 4, we can estimate the counterreaction barrier from 5-7-5 to bulklike structures, to be 1.68, 1.53, and 1.12 eV/dimer for Bi, Sb, and As, respectively. These results suggest that the surface transformation rate toward the 5-7-5 configuration is faster than the suppression rate for Bi and Sb on the Si(001) surface in favor of the Bi- and Sb-nanowire formation, whereas As on Si(001) shows the opposite trend and, consequently, no nanowire formation.

The transformation pathway previously proposed [4] for the Bi/Si(001) nanowire formation involves the rotation of four atom pairs in the 2nd and 3rd layers (labeled 5-6 and 7-8 in this work), the removal of four central atoms (labeled 1 and 2 in this work), and the rebonding of the 1st- and 4th-layer Si atoms. This process makes the overall strain field tensile, while keeping all bonds saturated. However, the starting structure with two adjacent Bi ad-dimers sitting on top of the dimer row is 0.50 eV/Bi-dimer less stable than the (2×8) phase (see Table I) and, therefore, has no energetic reason to grow long and straight. There is also no reason for the two ad-dimers to remain adjacent. Moreover, it leads to a barrier larger than 2.6 eV to rotate the 2nd and 3rd layer atoms and a large energy loss to remove the central atoms. The ad-dimer twisting assisted process identified in the present *dynamic* simulations resolves these energetic conflicts. It lowers the energy barrier and makes the self-organization process of the nanowire formation on Si(001) both favorable and natural.

In summary, we have studied the process of group-V adatom nanowire formation on Si(001) from both energetic and kinetic points of view. We identify a new mechanism that involves the rotation of *six atom pairs* in the 2nd and 3rd layers. A dynamic ad-dimer twisting assisted process significantly reduces the energy barrier and leads to the

self-assembly of a long nanowire with a double-dimer line configuration. The results provide a detailed understanding of the atomistic origin and the dynamic transformation pathway for the nanowire formation process. This new mechanism may also be relevant in the formation of other odd-membered ring structures, such as those observed on As-terminated Ge(001) [8] and Sb/Ge(113) [20], and be used as a basis for describing self-organizing nanolithography on semiconductor surfaces.

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