Gold deposited on a Ge(001) surface: DFT calculations

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Abstract

The atomic geometry, stability and electronic properties of self-organized Au induced nanowires on a Ge(001) surface are investigated based on the density-functional theory in the generalized gradient approximation and the stoichiometry of Au. According to the formation energy and the simulated STM image, the Ge atoms substituted by the Au atoms have been confirmed as occurring at a Au coverage lower than 0.25 Ml. The STM image with single and double dimer vacancies looks like the Au atoms have penetrated the subsurface. The energetically favorable dimer-row arrayed structures at 0.50 Ml and 0.75 Ml Au coverages have a \(4 \times 1\), \(4 \times 2\) or \(c(8 \times 2)\) transition symmetry, which comprise a flat Au–Au homodimer row and an alternating various buckling phase Ge–Ge or Au–Ge dimer row. The \(c(8 \times 2)\) zigzag-shaped protruding chains of shallow-groove STM images are highly consistent with the observations, but a long-range order dimer-row arrayed structure formation requires sufficient mobile energy to complete mass transport of the substituted Ge atoms in order to avoid the re-adsorption of these atoms; otherwise a deep-groove structure reconstruction is sequentially formed. A quasi-1D electron-like energy trough aligns in the direction perpendicular to the nanowire of the dimer-row arrayed structure in the \(c(8 \times 2)\) phase on a 0.75 Ml Au/Ge(001) surface, which is contributed by the Au–Ge dimer rows and the subsurface Ge atoms below them. The bottom energy of the energy trough is consistent with angle-resolved photoemission spectroscopy studies (Schäfer et al 2008 Phys. Rev. Lett. 101 236802, Meyer et al 2011 Phys. Rev. B 83 121411(R)).

Keywords: low dimensional physics, semiconductor surface, metallic adsorbates, surface electronic phenomena, density functional theory calculations

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(Some figures may appear in colour only in the online journal)

1. Introduction

Exploring low-dimensional electronic properties of metal-adsorbed semi-conducting surfaces is an interesting subject in surface physics. In particular, the metal-adsorbed Si and Ge surfaces are known to exhibit various kinds of two-dimensional (2D) or one-dimensional (1D) structures, yielding flat-lying chains of only a few atoms in width and of large extent [1]. A prominent characteristic of 1D structures is the Peierls instability [2], the electronic instabilities in purely 1D metals accompanied by a periodic lattice distortion (PLD). It has been found that adsorption of Pt atoms on Ge (001) results in highly ordered arrays and lengths of several hundred nm nanowires that exhibit sharply localized states [3–12]. Recently, gold growing in a self-organized manner on the Ge (001) surface is another interesting issue [11–29].

The system comprising Au on the Ge (001) surface has been studied by several research groups because of its interesting electronic and physical properties. Wang and Altman showed that the Au deposition on Ge (001) leads to a \(4 \times 2\)
low-energy electron diffraction (LEED) pattern of well-ordered arrays of Au-induced nanowires [13, 14]. A dimer-row structure model was suggested; the white and gray chains in the scanning tunneling microscopy (STM) images are attributed to the Au–Au and Au–Ge dimer rows, respectively. A few years later, Schäfer et al. using a hot substrate deposition process, prepared a deposition of about 0.5 ML Au on a Ge sample kept at 775 K, and studied it via STM, scanning tunneling spectroscopy (STS), and angle-resolved photo-emission spectroscopy (ARPES) [11, 15]. They found that self-organized atomic Au chains grew on Ge(001) in a \((8 \times 2)\) long-range order with 1D metallic characteristics close to the Fermi level in the chain direction, but excluded the charge density wave (CDW) according to the energy distribution curves of the 1D electron pocket at 15 K because of no occurrence of gap opening or band back-folding [16]. Based on the STM images, Housselt et al. [17] suggested a giant missing-row (GMR) reconstruction with anti-ferromagnetically ordered buckled Ge dimers on the top wires and a \([1 \{1\}](\sqrt{3} \times \sqrt{3})\) R30° microfacet structure on the side facets. However, density functional theory (DFT) calculations confirm that the GMR model is energetically unfavorable [18]. The atomic structure of the Au/Ge(001) surface is a controversial issue because the STM images are strongly influenced by the shape of the STM tip [17] and the sample bias voltages [11]. The depth perpendicular to the nanowires suggested by Wang et al. [13], Schäfer et al. [15] and Gallagher et al. [19], separately, is consistent, only 0.3–1.3 Å. However, Schäfer et al. [11] also observed the deep groove nanowires of 4–5 Å depth, Housselt et al. [17] found it to be not less than 6 Å deep, Kockmann et al. [20] considered it to be about 5 Å, and Nakatsuji et al. [21] reported a depth ranging from 3.4–4.6 Å. On the other hand, an eightfold modulation superstructure alternating arrangement of the zigzag and the chevron unit structure protrusions along the chain was found in STM measurements at room temperature [22–24], and the absence of buckled Ge–Ge dimers with dangling bonds on the surface was indicated by x-ray photoemission spectroscopy (XPS) results [22]. The superstructure undergoes a second-order phase transition at the critical temperature of 585 K, while the underlying \((8 \times 2)\) structure remains unaffected [23]. The \((8 \times 2)\) nanowire domain grows only at temperatures between 585 K and 665 K, and starts to form 3D islands above 665 K [24].

Recently, a \((8 \times 2)\)-Au surface was prepared by depositing 0.75 ± 0.05 ML of Au onto a Ge surface held at 800 K. The anisotropy introduced by the atomic steps of the vicinal surface and the preferential etching of Si steps during Au deposition is sufficient to introduce a preferred growth direction for the \((8 \times 2)\)-Au phase. The Ge(001) \((8 \times 2)\)-Au terraces with chains parallel to the step direction are separated by steps an integer multiple of the double atomic layer height \((n \times 2.8 Å)\) [25]. This is consistent with the finding of Wang et al. [14] who pointed out that the double height step is prevalent following Au deposition. Furthermore, the results of spot profile analysis of the diffraction peaks obtained by low energy electron diffraction (SPA-LEED) [26] show that the vertical height correlation functions strongly enhance the structure steps with double and quadruple atomic layer heights on a gold-covered Ge(001) surface, and the quadruple height step structure is dominant even on a surface of the deposited Au coverage lower than 0.2 ML, which is the prevailing structure when the Au coverage exceeds 0.6 ML.

The possible surface structures have been discussed theoretically based on the DFT calculations [18, 27–29]. Sauer et al. [18] conducted total-energy and electronic-structure calculations on a number of candidate surface structures with Au coverages ranging between 0.25 and 1.00 ML. They concluded that no one structure model could explain all the experimental results reported. Recently, a giant Ge zigzag chain (g-Ge ZC) structure [28] with a quadruple atomic layer height step structure was suggested for 0.75 ML Au coverage, which displays \((8 \times 2)\) deep groove zigzag nanowire structure simulated STM images. This structure displays large corrugation and deep troughs between the nanowires as per the experimental observations [17, 20, 22, 23]. The top layer Ge and Au atomic disorder introduces the chevron units into the zigzag nanowire structure STM image [28]; this structure model smoothly explains the second-order phase transition occurring at the critical temperature of 585 K in the experiment [23, 24]. However, some experimental researchers [13, 30] considered that their samples of 0.75 ML Au coverage agreed with the theoretically lowest-energy structure AD/HD model suggested by Sauer et al. [18].

Additionally, whether the surface electronic structure is 1D [15, 16] or 2D [21, 30, 31] is also a cause of controversy. The g-Ge ZC structure displays an anisotropic 2D upward parabolic surface-state band at surface Brillouin zone (SBZ) boundaries [28], which is consistent with the ARPES spectra reported by Nakatsuji et al. [21, 32]; however, it is not consistent with the quasi-1D energy trough ARPES results reported by Schäfer et al. [15, 16]. In contrast, the structures of the Pt/Ge(001) [7–10, 12, 33, 34], In/Si(1 1 1) [35–37] and Au/Si(1 1 1) [38] systems have been revealed by DFT calculations, demonstrating the ability of DFT to interpret the experimental data, particularly the atomic and electronic structures in comparison with the STM images and ARPES results. Thus, the theoretical calculations using DFT on the Au/Ge (001) system, especially the AD/HD model, deserve to be further investigated.

In this work, Au deposited on a Ge (001) surface was studied based on DFT in the generalized gradient approximation (GGA) in order to reveal the atomic geometry and bonding of the resulting self-organized arrays of nanowires, and to understand their electronic properties. The theoretical methods used for the total energy calculations and simulated STM images are described in section 2. The structure models for the stoichiometry Au-induced reconstructions are studied in section 3. At very low Au coverage defect single and double dimer vacancies have been revealed. The energetically favorable dimer-row arrayed structural models with shallow grooves at 0.5 ML and 0.75 ML Au coverage are exposed and are found to be consistent with the observed STM images [13–15, 19, 25]. The electronic structures for various phases of the dimer-row arrayed structural models at 0.5 ML and 0.75 ML Au coverage have been calculated. The relation between the shallow-groove and deep-groove structures
Table 1. Relative surface formation energies per \(1 \times 1\) unit cell in GGA and LDA, \(\Delta \Omega_f^{\text{GGA}}\) and \(\Delta \Omega_f^{\text{LDA}}\) (meV), respectively, when an Au atom is deposited on a clean Ge(001) surface at a certain adsorption or substituted site (figure 1), \(x\).

| \(x\) | \(\Delta \Theta_{\text{Au}}\) | \(\Delta \Theta_{\text{Ge}}\) | \(\Delta \Omega_f^{\text{GGA}}\) | \(\Delta \Omega_f^{\text{LDA}}\) |
|-------|-----------------|-----------------|-----------------|-----------------|
|       | 0.0625          | 0.0625          | 9               | 16              |
|       | 0.0625          | 0.0625          | 9               | 16              |
|       | 0.0625          | 0.0625          | 12              | 40              |
|       | 0.0625          | 0.0625          | 12              | 40              |
|       | 0.0625          | 0.0625          | 12              | 40              |
|       | 0.0625          | 0.0625          | 12              | 40              |
|       | 0.0625          | 0.0625          | 12              | 40              |
|       | 0.0625          | 0.0625          | 12              | 40              |
|       | 0.0625          | 0.0625          | 12              | 40              |
|       | 0.0625          | 0.0625          | 12              | 40              |

\(*\) Final position is at the uTu position.

Note: The Au and Ge coverages, \(\Delta \Theta_{\text{Au}}\) and \(\Delta \Theta_{\text{Ge}}\), are given in units of a monolayer. In this work, negative values of \(\Delta \Theta_{\text{Ge}}\) indicate the reduction in Ge atoms after Au deposition.

are discussed. A summary and conclusions are provided in section 4.

2. Theoretical method

A repeated slab supercell was employed. In each slab, there were ten atomic layers of Ge, of which the dangling bonds of the bottom Ge layer were saturated by H atoms. The H and the bottom two Ge layers were fixed. A sub-monolayer of Au atoms was deposited on the top layer of the slab. The height of the supercell in the [001] direction was fixed at 30 Å, which is sufficiently large to prevent coupling between the slabs. The total energy calculations were performed by VASP code [39–41] based on DFT using a plane-wave basis set with 25.72 Ry (350 eV) cutoff energy. The Perdew–Wang (PW91) exchange-correlation function [42] for GGA was adopted. The electron–ion interaction pseudopotentials were specified using the projector augmented-wave (PAW) method [43] in which the 3d, 4s and 4p electrons of the Ge atom and the 5d and 6s electrons of the Au atom are considered as valence. For bulk Ge, the optimal lattice constant of \(a_0\) is 5.7585 Å, which is about 1.6% larger than the experimental value, 5.6575 Å, due to the under-binding for GGA treatment. The irreducible Brillouin zone was sampled with a 2 \(\times\) 2 \(\times\) 4 Monkhorst and Pack mesh for an 8 \(\times\) 8 \(\times\) 8 surface unit cell. Structure optimization was performed until the residual force acting on each atom was less than 0.01 eV Å\(^{-1}\).

According to the Tersoff–Hamann approach [44, 45], the tunneling current in STM is proportional to the local density of states (LDOS) near the Fermi level of the sample at the position of the tip. In the following discussion, a series of simulated STM images was produced by extracting the contours of various iso-surfaces of the LDOS to simulate different tunneling currents in the constant height model, and the lateral height profile of an iso-surface of LDOS is used to estimate the apparent height that is measured with the constant current STM mode in the experiments.

3. Results and discussion

The relative surface formation energies of a certain surface atomic structure, \(x\), are calculated with regard to the clean Ge(001) \(b(2 \times 1)\) surface using the following expression

\[
\Delta \Omega_f = E_x - E_{\text{Ge}(001)} - \Delta N_{\text{Au}} E_{\text{Au}} - \Delta N_{\text{Ge}} E_{\text{Ge}}
\]

where \(E_x\) is the total energy of the relaxed structure, \(E_{\text{Ge}(001)}\) is the total energy of the clean Ge(001) \(b(2 \times 1)\) surface, \(E_{\text{Au}}\) (\(E_{\text{Ge}}\)) is the bulk energy per Au (Ge) atom, and \(\Delta N_{\text{Au}}\) (\(\Delta N_{\text{Ge}}\)) is the difference in the number of Au (Ge) atoms between the relaxed structure and the clean Ge(001) geometry.

3.1. \(\Theta_{\text{Au}} = 1/16\) Ml

As listed in table 1, the relative surface formation energies for 1/16 Ml Au coverage adsorbed at various positions of the \(c(4 \times 2)\)-Ge(001) surface are positive in GGA except at the uTu position, which is the middle point of the trough between two dimer rows and two upper buckling Ge atoms, as shown in figure 1. However, the surface formation energies in LDA are all positive. This indicates that the Au atoms adsorbed on a Ge (001) surface are unstable no matter where they are. In fact, as listed in table 1, the Au atom prefers to substitute the Ge atom to form a local...
Au–Ge heterodimer (AGD), and the Au substituted for the lower Ge atom, figure 2(a), is more stable than that substituted for the upper Ge atom.

Similar to the low coverage Pt/Ge(0 0 1) case, the AGD tends to flatten out. The bond length of the AGD is 2.572 Å with a small buckling angle of 9.6° in comparison with 2.568 Å and 19.5° for the Ge dimer of a clean 4 × 2-Ge(0 0 1) surface. Figure 2(b) shows the simulated STM images of the local AGD at various sample biases. In contrast to the bright Ge atomic protrusions, the vague Au STM images in both the occupied and unoccupied states look like the Au atoms penetrated the subsurface, similar to the LEED and PES experimental observations at very low Au coverage [13, 14, 19, 22]. The image of the Ge dimers adjacent to the AGD in the same dimer row is not different from the unperturbed area at occupied states. However, in the unoccupied state at low sample bias voltages, the STM image of the Ge dimer adjacent to the AGD displays a vacancy at the lower Ge dimer atom and a weak protrusion at the upper Ge dimer atom at \( V_s = +0.25 \) V and two asymmetric protrusions at \( V_s = +0.5 \) V; this is in contrast to the unperturbed area where the bright protrusions only present at the lower Ge dimer atoms similar to the clean Ge(0 0 1) surface [46]. This result implies that the surface band of the upper Ge dimer atom is adjacent to the AGD crossing the Fermi level, while simultaneously the charge transfer reduces the buckling angle of the AGD to 9.6° and enhances its own buckling angle to 22.0°.

3.2. \( \Theta_{Au} = 1/8 \) Ml

As the coverage of deposited Au continuously increases to 1/8 Ml, the local AGDs could be arranged as a local aligned out-of-phase Au–Ge pair (AGD pair), an alternating buckled AGD zigzag chain (AGZC-8 × 2), an in-phase buckled AGD chain (AGDC-8 × 1), or two Au atoms substituting for a Ge dimer to form a local Au–Au homodimer (AAD) as shown in figure 2(c). Their surface formation energies are listed in table 2 which shows that the AAD is indeed more energetically favorable than forming two AGDs, no matter how they are configured. Furthermore, comparing table 2 with table 1, two Au atoms substituting for a Ge dimer to form an AAD or substituting for two Ge dimers to form two AGDs is more stable than the clean Ge(0 0 1) surface.

The bond length of the AAD is 2.891 Å, similar to the atomic distance of the Au bulk, 2.952 Å in GGA. At the same time, the bond lengths of the adjacent Ge dimers change to 2.557 and 2.570 Å with buckling angles of 20.1° and 19.5°, respectively, as shown in figure 2(c). The strain effect on the adjacent Ge dimers on the same dimer row is stronger than that on different dimer rows. Figure 2(d) shows that the simulated images look like the observed vacancy-riddled Ge(0 0 1) surface at a low Au coverage deposition [12, 13, 19, 22]. In the occupied states, two close faint lumps at the local AAD look like a missing dimer defect; an apparent vacancy image of the local AAD presents at \( V_s = -0.25 \) V. The faint AAD lump STM pattern also displays at low sample bias in the
unoccupied states, but becomes a cloudy oblong feature at \( V_s = +0.75 \text{V} \) resulting from the unoccupied \( \pi^* \) antibonding state. At \( V_s = +0.50 \text{V} \), the STM image with two bright protrusions is clearly present at the adjacent Ge dimers on the same dimer row. Comparing figures 2(b) and (d), the STM image intensity of the adjacent upper Ge dimer atom at 1/8 MI is higher than that at 1/16 MI in the unoccupied state. This result indicates that the strain effect induces more charges of the upper Ge dimer atoms transferred to the adjacent AAD in contrast with the case of 1/16 MI Au deposition.

### Table 3. Relative surface formation energies per 1 × 1 unit cell in DFT-GGA, \( \Delta f_T^{\text{GGA}} \) (meV), for various surface structural models, x, when 1/4 MI Au atoms are deposited on the Ge(0 0 1) surface.

| x               | Translation symmetry | \( \Delta \Theta_{\text{Ge}} \) | \( \Delta f_T^{\text{GGA}} \) |
|-----------------|----------------------|---------------------------------|-----------------------------|
| TDC [32]        | 4 × 2                | −0.25                           | 52                          |
| IPGNW [33]      | 4 × 2                | 0                               | 116                         |
| ALC (T1 + T1)   | 4 × 2                | 0                               | 208                         |
| ALC (uTu + iTd) | 4 × 2                | 0                               | 76                          |
| PNW [10]        | 4 × 2                | −0.125                           | 214                         |
| PNW\(^4\)       | 4 × 2                | −0.125                           | 226                         |
| AADR            | 8 × 2                | −0.25                            | −72                         |
| Au–Au pair      | 8 × 2                | −0.25                            | −55                         |
| Au–Au 8 × 2–1   | 8 × 2                | −0.25                            | −55                         |
| Au–Au 8 × 2–2   | 8 × 2                | −0.25                            | −55                         |
| AGDR + GGDR     | 4 × 2                | −0.25                            | −37                         |
| a-Au–Ge DR      | 8 × 1                | −0.25                            | −37                         |
| b-Au–Ge DR      | 8 × 1                | −0.25                            | −39                         |

*The missing upper Ge dimer atom of every second Ge dimer of every second dimer row in the Pt nanowire (PNW [10]) model is replaced by the down Ge dimer atom.

**Note:** Some of the structure models are shown in figure 3.

Because there are credible nanowire structure models that have been accepted on the nanowire Pt/Ge(001) surface, when the coverage of Au increases to 1/4 MI, intuitively, the atomic reconstructed structural models of the Pt/Ge(001) surface including the tetramer-dimer-chain (TDC) [33], the imbedded Pt chain induced Ge nanowire (IPCNW) [34], the single-atom-wide Au linear chains (ALC) positioned in the troughs [15] and the Pt nanowire (PNW) [10] structure models were examined. The former two are energetically favorable structures on the Pt/Ge(001) surface at 1/4 MI Pt deposition [12], but the Pt atoms were replaced with Au atoms here. Unfortunately, these structures are unstable according to the positive surface formation energies in GGA as listed in table 3 in which the result of the TDC model is the same as the report of Sauer et al. [18]. This result implies that the hints of the atomic structure model of the Pt/Ge(001) system are not entirely appropriate when Pt/Ge(001) comes to the Au/Ge(001) system because the electron count plays an important role in stabilizing many semiconductor surfaces. Therefore, the surface atomic structure model of the Au/Ge(001) surface should be different from that of the Pt/Ge(001) surface, even though the atomic number difference between Au and Pt is only one. In fact, many reconstructed Au/Ge(001) surfaces have been inspected but are not shown here because they have positive surface formation energies, which include directly adsorbing Au atoms on the top of the Ge dimers or in the trench without substituting for any Ge atoms.

If the Au atoms successively substitute for the Ge atoms as mentioned above with increasing deposited Au coverage, then the possible reconstructions built by the AAD and AGD structural elements are shown in figure 3. According to the relative surface formation energies in GGA, table 3, the reconstructed structures comprised of AADs as shown in figures 3(a)–(d) are energetically more favorable than those comprised of AGD as shown in figures 3(e)–(h), and the side by side AADs arrangement as a local Au–Au homodimer row (AADR), figure 3(a), is more stable than two aligned AADs, figure 3(b), or two distant AADs, figures 3(c) and (d). The strain effect between the Au–Au homodimers of AADR is obvious, and the bond length of the local flat AAD is enlarged to 3.006 Å, which is longer than that of 1/8 MI Au coverage, 2.891 Å. Figures 4(a) and (b) show that the image intensities of the AADRs are weaker than the neighboring Ge–Ge dimer rows (GGDRs) in the sample bias range of \(-1.00 \text{V} \leq V_s \leq +0.75 \text{V} \) because of the rare density of states of Au within the energy window. The local AADR simulated STM images look like a two-atom-wide missing dimer trench aligned in the [1 1 0] direction.

In fact, the configuration of two side-by-side AADs is often observed on the Au/Ge(001) surface at Au coverage of less than 0.25 MI. Figures 4(c) and (d) show the simulated STM images of two local side-by-side AADs for an 8 × 4 supercell in the occupied and unoccupied states, respectively. The images look like a double dimer vacancy on the Ge(001) surface, which is consistent with the observations, for example, figure 1 of [14], and figure 5 as noted in [22]. It is worth noting that the ad-dimers are always found around the double dimer vacancy; for example, figure 1 of [14].

### 3.3. \( \Theta_{\text{Au}} = 1/4 \text{ MI} \)

Because there are credible nanowire structure models that have been accepted on the nanowire Pt/Ge(001) surface, when the coverage of Au increases to 1/4 MI, intuitively, the atomic reconstructed structural models of the Pt/Ge(001) surface including the tetramer-dimer-chain (TDC) [33], the imbedded Pt chain induced Ge nanowire (IPCGNW) [34], the single-atom-wide Au linear chains (ALC) positioned in the troughs [15] and the Pt nanowire (PNW) [10] structure models were examined. The former two are energetically favorable structures on the Pt/Ge(001) surface at 1/4 MI Pt deposition [12], but the Pt atoms were replaced with Au atoms here. Unfortunately, these structures are unstable according to the positive surface formation energies in GGA as listed in table 3 in which the result of the TDC model is the same as the report of Sauer et al. [18]. This result implies that the hints of the atomic structure model of the Pt/Ge(001) system are not entirely appropriate when Pt/Ge(001) comes to the Au/Ge(001) system because the electron count plays an important role in stabilizing many semiconductor surfaces. Therefore, the surface atomic structure model of the Au/Ge(001) surface should be different from that of the Pt/Ge(001) surface, even though the atomic number difference between Au and Pt is only one. In fact, many reconstructed Au/Ge(001) surfaces have been inspected but are not shown here because they have positive surface formation energies, which include directly adsorbing Au atoms on the top of the Ge dimers or in the trench without substituting for any Ge atoms.

If the Au atoms successively substitute for the Ge atoms as mentioned above with increasing deposited Au coverage, then the possible reconstructions built by the AAD and AGD structural elements are shown in figure 3. According to the relative surface formation energies in GGA, table 3, the reconstructed structures comprised of AADs as shown in figures 3(a)–(d) are energetically more favorable than those comprised of AGD as shown in figures 3(e)–(h), and the side by side AADs arrangement as a local Au–Au homodimer row (AADR), figure 3(a), is more stable than two aligned AADs, figure 3(b), or two distant AADs, figures 3(c) and (d). The strain effect between the Au–Au homodimers of AADR is obvious, and the bond length of the local flat AAD is enlarged to 3.006 Å, which is longer than that of 1/8 MI Au coverage, 2.891 Å. Figures 4(a) and (b) show that the image intensities of the AADRs are weaker than the neighboring Ge–Ge dimer rows (GGDRs) in the sample bias range of \(-1.00 \text{V} \leq V_s \leq +0.75 \text{V} \) because of the rare density of states of Au within the energy window. The local AADR simulated STM images look like a two-atom-wide missing dimer trench aligned in the [1 1 0] direction.

In fact, the configuration of two side-by-side AADs is often observed on the Au/Ge(001) surface at Au coverage of less than 0.25 MI. Figures 4(c) and (d) show the simulated STM images of two local side-by-side AADs for an 8 × 4 supercell in the occupied and unoccupied states, respectively. The images look like a double dimer vacancy on the Ge(001) surface, which is consistent with the observations, for example, figure 1 of [14], and figure 5 as noted in [22]. It is worth noting that the ad-dimers are always found around the double dimer vacancy; for example, figure 1 of [14].

### 3.4. Dimer-row arrayed structural models

#### 3.4.1. \( \Theta_{\text{Au}} = 1/2 \text{ MI} \)

For the 0.50 MI Au deposition, some simple structural models were firstly checked. Two Au chain models, the Pt dimer chain model (PDC [3]) and the zigzag Au chain model (GC3 [18]), were examined, in which the Au chain is located in the trough between two dimer rows. In the relaxed PDC structure, the Au atom finally left its tentative linear dimer chain position. In the GC3 structure, the zigzag Au chains could be out of phase with c(8 × 2) surface translation symmetry or in phase with 4 × 2 translation symmetry, but the formation energies of both phases are very close; this result indicates that the inter-chain interaction among the zigzag Au chains is very weak. Table 4 shows that these two models are energetically unfavorable. If the Au atoms have been substituted for the Ge atoms with increasing Au coverage as mentioned above, the energetic favorable AADR should be widely distributed on the Au/Ge(001) surface; thus, what is the best arrangement of the AADRs and GGDRs on the surface? It was found that at
0.50 Ml Au coverage, alternating AADR and GGDR formed as a (AADR + GGDR) dimer-row arrayed structure surface is more stable than alternating double AADRs and double GGDRs formed as a (2AADR + 2GGDR) double-dimer-row arrayed structure surface. The nanowire spacing of the (AADR + GGDR) surface is 16.28 Å in the direction perpendicular to the row. The buckling of the Ge dimers between the adjacent GGDRs, separated by an AADR interval, could be in phase with 4 × 1 or 4 × 2 surface translational symmetry as shown in figures 5(a) and (b), or an antiferromagnetic structure with c(8 × 2) surface translational symmetry as shown in figure 5(c). The total energy difference for an 8 × 2 supercell between the 4 × 1 and 4 × 2 phases is 321.0 meV, but that between the 4 × 2 and c(8 × 2) phases is only about 1.8 meV. Because this magnitude of the latter is beyond the accuracy of the DFT calculations, this result indicates that the 4 × 2 and c(8 × 2) phases should coexist on the surface, and/or a phase transition could be induced by thermal fluctuation. Apparently,
both of the $4 \times 2$ and $c(8 \times 2)$ surface reconstructions were observed by Wang et al. [13], and the flip-flopping dynamic behavior of the Ge dimers induced by thermal fluctuation was also observed by Mocking et al. [47]. The bond lengths of the flat Au–Au dimers of the (AADR + GGDR) structures are in the range of 3.003–3.008 Å, and those of the buckled Ge–Ge dimers of the $4 \times 2$ and $c(8 \times 2)$ phases are 2.568 and 2.570 Å depending on the buckling phase of the neighboring Ge–Ge dimers as shown in figures 5(b) and (c), but the Ge–Ge dimer bond length of the $4 \times 1$ phase shrinks slightly to 2.502 Å.

Figure 5(d) displays the simulated STM images of the $4 \times 1$ phase. The single-atom-wide bright protruded linear chains are separated by the faint two-atom-wide nanowires at negative sample biases; the former are instead of the asymmetric two-atom-wide protruded linear chains at positive sample biases. The faint two-atom-wide nanowire and the bright protruded linear chain images result from the AADRs and the buckled Ge–Ge dimers of the GGDRs, respectively. The bright protruded zigzag chains of the $4 \times 1$ phase becomes the protruding zigzag chains in the $4 \times 2$ and $c(8 \times 2)$ phases as shown in figures 5(e) and (f), and their occupied and unoccupied state images have an out-of-phase shift. These bright protruded zigzag chains and the faint nanowires in the simulated STM images should be assigned to the white chains and the gray chains of the observed STM images (figure 2 as noted in [13]), respectively; however, this is in contrast to the assignment of Wang et al [13] who considered the white and gray chains in the STM images as being the Au–Au and Au–Ge dimer rows, respectively. Careful inspection of the experimental STM image, figure 2 noted in [13], finds a part of the gray chain image with buckling similar to the white chain, which is different from the simulated STM image of the pure (AADR + GGDR) structure.

| $x$            | Translation symmetry | $\Delta \Theta_{Au}$ | $\Delta \Theta_{Ge}$ | $\Delta \Omega_{GGA}$ |
|---------------|----------------------|----------------------|----------------------|-----------------------|
| PDC [3]       | $4 \times 2$         | 0.50                 | -0.25                | 52                    |
| GC3 [18]      | $4 \times 2$         | 0.50                 | 0                    | 59                    |
| $c(8 \times 2)$ | 0.50                 | 0                    | 59                    |
| AADR + GGDR   | $4 \times 1$         | 0.50                 | -0.50                | -89                   |
| $c(8 \times 2)$ | 0.50                 | -0.50                | -109                 |
| 2AADR + 2GGDR | $8 \times 1^a$       | 0.50                 | -0.50                | -90                   |
| $8 \times 2$  | 0.50                 | -0.50                | -83                   |
| AADR + AGDR   | $4 \times 1$         | 0.75                 | -0.75                | -110                  |
| $c(8 \times 2)$ | 0.75                 | -0.75                | -110                 |
| EBD [18]      | $c(8 \times 2)$      | 0.75                 | -0.25                | -113                  |
| PINW [7]      | $4 \times 2$         | 0.75                 | -0.50                | 110                   |
| MTL           | $2 \times 1$         | 1.00                 | -1.00                | -180                  |

$a$The neighboring aligned Ge–Ge dimers have in-phase buckled angles.
$b$The neighboring aligned Ge–Ge dimers have out-of-phase buckled angles.
We further checked the lateral profile of the partial LDOS iso-surface contour to evaluate the apparent height in the constant current STM mode. It shows that the $4 \times 2$ and $c(8 \times 2)$ phases have an apparent height of about 1.1 Å between the upper Ge atom of GGDR and the Au atom of AADR at $-1.5$ V sample bias in spite of the atomic height between the center of the buckled Ge dimer and the flat AADR being only 0.052 Å, and the distance between the upper Ge atom of the GGDR and the Au atom of the AADR being 0.383 Å in the [0 0 1] direction. This is attributed to an STM measured apparent height not being entirely determined by the topographic structural height difference. The evaluated apparent height is consistent with the experimental STM measured results, for example, 1.0 Å at $V_s = -1.5$ V [13], 1.3 Å at $V_s = -2.1$ V [15] and typically ~1–2 Å depending on the tunneling conditions [11].

In fact, the total energy difference between the optimal structures of (2AADR + 2GGDR) and (AADR + GGDR) is only 0.8 meV per $8 \times 2$ supercell, which is also beyond the accuracy of the DFT calculations. The double two-atom-wide nanowire feature is often observed at the edge of the terrace in the STM images at higher Au deposition; for example, interdigitation of the white chains indicated in figure 8(a) of [12], figure 6(b) of [14], and the double wires indicated in figure 1 of [47].

3.4.2. $\Theta_{Au} = \frac{3}{4}$ Ml. When the concentration of deposited Au exceeds 0.5 Ml, if the added Au atoms continuously replace the lower Ge atoms of GGDRs to form Au–Ge heterodimers, a surface comprised of alternating arrays of AADR and Au–Ge heterodimers (AGDR) is formed at 0.75 Ml Au coverage. Similar to the case of 0.5 Ml Au coverage, the translation symmetry of this surface could be $4 \times 1$ (figure 6(a)), $4 \times 2$ (figure 6(b)) or $c(8 \times 2)$ (figure 6(c)) according to the buckling phase among the neighboring AGDRs. The structure difference between the $4 \times 2$ and $c(8 \times 2)$ phases is that the neighboring AGDRs shifted a half of the periodic length in the $c(8 \times 2)$ phase. The $4 \times 2$ phase corresponds to the AD/HD model suggested by Sauer et al. [18]. As listed in table 4, these three phases have the same formation energies considering the accuracy of the DFT calculations; actually, the total energy difference between the $4 \times 2$ and $c(8 \times 2)$ phases is only 1.6 meV per $8 \times 2$ surface unit. This result indicates that these three surface phases could coexist in a real system.

The periodicity of the nanowires of the (AADR + AGDR) structure is 16.28 Å ($=4a$) perpendicular to the nanowire, and 8.14 Å ($=2a$) along the nanowire for the $4 \times 2$ phase. The Au–Ge bond lengths of AGDR of the $4 \times 2$ and $c(8 \times 2)$ phases are 2.583 Å with a buckling angle of 13.2° which is weaker than the tilted angle of the Ge dimer of the (AADR + GGDR) structure at 0.50 Ml Au coverage, 19.7°. The Au–Au bond lengths of the flat AADRs are in the range of 2.981–3.011 Å, depending on the tensile modulation effect resulting from the inter-nanowire interactions between the AADs and the neighboring AGDs; this effect is apparent in the $c(8 \times 2)$ phase.

For the $4 \times 1$ phase, the simulated STM images of the (AADR + AGDR) structure, figure 6(d), have similar...
features in comparison with the (AADR + GGDR) structure, figure 5(d). For the 4 × 2 and c(4 × 2) phases of the (AADR + AGDR) structure, figures 6(e) and (f), the images of alternating the protruded zigzag chain and the faint trench look like the (AADR + GGDR) structure. The faint trenches are given by the AADRs, and the bright protruding zigzag chains are contributed by the Ge atoms of the Au–Ge heterodimers. By checking further, it was found that the simulated STM image of the (AADR + AGDR) structure is different from that of the (AADR + GGDR) structure; there are no phase shifts between the occupied state and unoccupied state of the (AADR + AGDR) structure images. The lateral amplitudes of the zigzag chain images, indicated by the ‘Δ’ symbol in figures 6(e) and (f), depend on the sample biases; it is clearly smaller at negative sample bias than at positive sample bias. The apparent height is about 1.0 Å at −1.5V sample bias, and this value is consistent with the observation by Gallagher et al [19].

Because the STM images of both the (AADR + GGDR) and (AADR + AGDR) structures have a similar feature of zigzag chain protrusions, and have nearly equal surface formation energies, the surface could present a mixed structure on the Au/Ge(001) surface when the coverage of deposited Au is in the range of 0.50 ML−0.75 ML. This result explains why the experimental STM images have similar zigzag protrusion characteristics at 0.50 ML [13–15] and 0.75 ML [19] Au coverages. Based on the above discussion, the dimer-row arrayed structure with double atomic layer height could be a candidate for the observed shallow-groove STM images [13–15, 19, 25]. However, except for the report of Wang et al [13, 14], the dimer rows were not observed in the grooves of the shallow-groove STM images [15, 19]. On the other hand, it is apparent that to gain a long-range dimer-row arrayed structure domain it must be accompanied by sufficient mobile energy to complete mass transport of the substituted Ge atoms. At insufficient temperatures and high exposure of Au, there is not enough mass transport energy to remove the substituted Ge atoms which could let these substituted Ge atoms recombine with the neighboring Au or Ge atoms in place and form a giant reconstructed structure. Therefore, a large area of the long-range order shallow-groove dimer-row arrayed structure is not commonly observed. Actually, the area of the shallow-groove structure is small in comparison with the large-scale deep-groove structure on a 0.75 ML Au/Ge(001) surface, as shown in figures 3 and 4 of [25]. This argument is also supported by the fact that the missing top layer (MTL) structure is the lowest surface formation energy in the range of $\Theta_{Au}$ between 0.0 ML and 1.0 ML as listed in table 4, but its STM images have not yet been observed. The MTL structure is similar to the (Na, K)/Si(111) surface in which one half of the bilayer Ge atoms of the Ge(001) surface is replaced by Au atoms [48]; this structure also needs mobile energy to complete transportation of the substituted Ge atoms.

Recently, a structure model has been suggested on a 0.75 ML Au/Ge(001) surface, in which the substituted Ge atoms recombine with the Au atoms. Figure 7(a) shows the c(8 × 2) g-Ge ZC structure reconstruction where the nanowires are separated by 16 Å with a quadruple atomic layer height [28]. This structure model has large corrugations and deep troughs, and successfully explains the V-W STM features [22–24] and the second-order phase transition [23]. Figure 7(b) shows the simulated STM images of a 4 × 8 supercell at various sample biases. The STM image pattern strongly depends on the sample bias as per experimental observation [20]. A deep-groove zigzag nanowire pattern presents at $|V_{s}| > 0.3$V, but the nanowire looks like a shallow-groove linear nanowire at very low sample bias. The linear nanowire feature of the simulated STM images at low sample bias is similar to the experimental observation as noted in figure 2(a) of [15].

Experimentally, the nanowires parallel to the step direction separated by various step heights with a majority of 5.6 Å and a minority of 2.8 Å, coexist at 1.6V sample bias as presented in figure 3 of [25]. This result is consistent with the recent finding of SPA-LEED as noted in figures 5(d) and (e) of [26] in which it was found that (i) the vertical height correlation function of the quadruple atomic layer height structure strongly increases with increasing Au coverage on a gold-covered Ge(001) surface, and the quadruple atomic height step structure is dominant at the deposited Au beyond 0.6 ML. (ii) Despite the double atomic layer height structure not being the prevailing structure, the double atomic layer height correlation function $C_2$ increases with increasing Au coverage [26].
Thus, the double atomic layer height structure is not usually observed all over the surface; it could be considered as a local defect structure but should not be ignored. As stated in the above discussion, the g-Ge ZC structure model can undoubtedly be considered as the majority structure with the nanowires of 5.6 Å step height, which atomic and electronic structures are consistent with experiments for the deep-groove structure, but this structure model cannot explain the minority nanowire structure of 2.8 Å step height. In order to check the inference of whether the dimer-row arrayed structure can be considered as the double atomic layer height defect when the Au coverage exceeds 0.5 ML or not, the electronic structures of the dimer-row arrayed structure are calculated in the following.

3.5. Electronic structures

To fully understand the electronic structures of the (AADR + GGDR) and (AADR + AGDR) structures, the electronic structure of the 4 × 1, 4 × 2 and c(8 × 2) phases are calculated. Figures 8(a)–(c) show the electronic structures of the dimer-row arrayed structure on a 0.50 ML Au/Ge(0 0 1) surface for the 4 × 1, 4 × 2 and c(8 × 2) phases, respectively, although the 4 × 1 phase is not the energetically favorable structure in the (AADR + GGDR) structure. For the 4 × 1 phase, two 1D metallic surface states S1 and S2 bands cross the Fermi level, $E_F$, at about the $Y_4$ and $Y_4'$ points, which are one half of the first SBZ boundaries, the $JY_28$ and $Y_8$ lines. These two surface-state energy bands originate from the Au homodimers of the AADR (solid orange circles) and the second layer Ge atoms below them (solid black circles). This indicates that the AADRs of the 4 × 1 phase surface are metallic in the 1 × periodic direction. Figure 8(a) also shows that the surface-state bands S3, S4 and S5 display the semiconducting property with a direct bandgap of 347.0 meV at the $\Gamma$ point, which are contributed by the Ge–Ge dimers (open blue circles) of the GGDR and the subsurface Ge atoms below them (solid blue circles). It is worth noting that the S3 band couples with the S1 band in the 1 × periodic direction ($JY_28$ line) around $E_F + 0.80$ eV, and the S4 band couples with the S2 band in the perpendicular to the 1 × periodic direction ($YY_8Y_8'$ line) around $E_F - 1.05$ eV; this indicates that in these energy ranges, the inter-nanowire interaction between the AADRs and GGDRs plays an important role in the electrical transport.

Because of the occurrence of the band back-folding in the 4 × 2 phase, figure 8(b) shows that the S1 and S2' bands cross the Fermi level on the $JY_28$ and $JY_8$ lines, and two very small energy bandgaps were opened at the SBZ boundaries in the 4 × periodic direction, the $YY_8Y_8'$ line. Since the energy gaps are extremely small (supplementary figure S1 (stacks.iop.org/JPhysCM/28/435001/mmedia)), it is difficult to observe with the naked eye in figure 8(b). One of the bandgaps is contributed by the S1 band couples with the S1 band situated at just below the Fermi level, which gap has a width of 0.50 meV at the $Y_4$ point and 0.37 meV at the $Y_4'$ point, respectively; accordingly, the S1 band...
exhibits an electron-like property. The other gap is contributed by the $S_2$ and $S'_2$ bands situated above the Fermi level, which gap of 0.13 meV displays very slight dispersion on the $\overline{Y}Y_4$ line; thus, near the Fermi edge window, the surface-state $S'_2$ band evidently displays a 1D electron-like property along the nanowire, but behaves with a hole-like property perpendicular to the nanowire. Consequently, the AADR displays a semimetallic property in the $4 \times$ periodic direction, and a metallic property in the $2 \times$ periodic direction. On the other hand, the surface-state $S_3$ band contributed by the GGDRs displays very slight energy dispersion in the $4 \times$ periodic direction, the $J_2 \Gamma$ line, and crosses the Fermi level at the $0.33 J_2 \Gamma$ line from the $\Gamma$ point. In the $2 \times$ periodic direction, on the $\overline{Y}Y_4'$ and $JY_24'$ lines separately, this surface-state band displays upward parabolic dispersion and couples with the $S_1$ band. Consequently, this band looks like an upward energy trough with an energy bottom crossing the Fermi level on the $J_2 \Gamma$ line, and exhibits an electronic-like property. Therefore, based on the dimer-row arrayed structure model, the electronic structure of the GGDRs on a 0.50 ML Au/Ge(0 0 1) surface indeed exhibits the metallic property in the $4 \times 2$ phase.

Because the $4 \times 2$ and $c(8 \times 2)$ phases have approximate formation energies, once the surface structure from $4 \times 2$ transforms into the $c(8 \times 2)$ phase, the surface tensile effect apparently acts on the Au–Au homodimers as mentioned above. As shown in figure 8(c), this effect raises the $S_1 (S'_1)$, $S_2 (S'_2)$ and $S_3$ bands on the $\overline{Y}Y'$ line, but only raises the $S_1$, $S_2 (S'_2)$ and $S_3$ bands and lowers the $S'_1$ band on the $JY_4'$ line. Therefore, the GGDR exhibits a semiconducting property with a direct gap of 274.0 meV in the $c(8 \times 2)$ phase. It is worth noting that the $S_1 (S'_1)$ and $S_2 (S'_2)$ bands exhibit linear and symmetric dispersion with respect to the middle line of the $YY'$ line, similar to the Dirac-like band dispersion. Two bandgaps of 2.69 meV and 1.28 meV were opened at the $L$ point, the middle point of the $\overline{Y}Y'$ line; one is just at the Fermi level and the other is located above the Fermi level. As can be clearly seen in the inset of figure 8(c), the constant energy surface contour of the $S'_1$ band displays nearly no dispersion perpendicular to the nanowire at $E_F$. This indicates that the $S'_1$ band, mostly contributed by the subsurface Ge atoms below the AADRs, keeps the quasi-1D metallic property at the Fermi level.

The LDOS of the $c(8 \times 2)$ structure at the Fermi edge, $(E_F = 0.1) \text{eV} < E < (E_F + 0.1) \text{eV}$, mainly comes from the AADRs and the subsurface Ge atoms beneath them, but not from the GGDRs. This result is in contrast to the $4 \times 2$ phase in which the LDOS at the Fermi energy window is contributed by both the AADRs and GGDRs. However, because of the coexistence of both the $4 \times 2$ and $c(8 \times 2)$ phases, from the viewpoint of the system’s total energy as mentioned above, the dominant electronic conductivity within this small energy window at the Fermi level on a mixed defect structure could be principally contributed not only by the AADRs and the subsurface Ge atoms, but also by the GGDRs, depending on the local atomic surface structure.

**Figure 9.** Electronic structures of the dimer-row arrayed structure models for the (a) $4 \times 1$, (b) $4 \times 2$ and (c) $c(8 \times 2)$ phases at 0.75 ML Au deposited on a Ge(001) surface. The open orange circles, open blue circles, and solid blue circles represent the bands contributed by the Au and Ge atoms of the Au–Ge heterodimers, and their underlying Ge atoms. The solid orange circles and solid black circles represent the bands contributed by the Au–Au homodimers and their underlying Ge atoms. The radii of circles are proportional to their weight of contribution. The insets of (b) and (c) are the constant-energy surface mapping at the Fermi level for the $4 \times 2$ and $c(8 \times 2)$ phases.
On a 0.75 ML Au/Ge(001) 4 × 1 surface, similar to the 0.50 ML Au coverage surface, the S1 (S2) band originates from the AADRs (indicated by solid orange circles in figure 9) and the second layer Ge atoms (solid black circles), which crosses the Fermi level at the 0.52 (0.53) of the ΥΓ length from the Υ point and 0.48 (0.56) of the ΓM length from the Γ point as shown in figure 9(a); these crossing points are near the Υ and Γ points. Therefore, the surface-state S1 and S2 bands have a quasi-1D metallic property. In addition, there are three surface-state bands, S3, S4 and S5, around the Fermi level, which are contributed by the AGDRs (open orange and open blue circles) and the subsurface Ge atoms below the AGDRs (solid blue circles). One of these surface bands, the S1 band crossing the Fermi level at 0.44 of the ΓM (ΓS) length from the Γ (Γ′) point, shows quasi-1D metallic behavior. This surface band apparently couples with the bands contributed by the subsurface Ge atoms beneath the AADR (solid black circles) around EF = 1.10 eV near the SBZ boundaries, the Υ and Γ points.

Figure 9(b) shows that the S1 and S2 bands of the AADRs strongly couple with the second layer Ge atoms (solid black circles) on the Y4 line when the surface structure transfers from the 4 × 1 phase to the 4 × 2 phase on a 0.75 ML Au/Ge(001) surface. Because of the occurrence of the band back-folding, two very small bandgaps were opened at the SBZ boundaries on the Y4Y line (supplementary figure S2). Since these energy gaps in figure 9(b) are extremely small, they are difficult to observe with the naked eye. One of these two gaps is opened by the S2 and S′ 2 bands, which have a gap width of 1.25 meV at the Y4 point and 1.38 meV at the Γ4 point; this gap displays nearly no dispersion in the Y4 direction above the Fermi level. Similarly, the other gap is opened by the S1 and S′ 1 bands, which has a gap width of 0.12 meV at the Y1 point above the Fermi level and 0.40 meV at the Y4 point below the Fermi level; thus, this gap crosses the Fermi level on the Y4Y line. Therefore, a 2D hole-like packet is formed near the Y1 point, which is indicated by black circles in the inset of figure 9(b).

Strong inter-nanowire interactions between the AGDRs and AADRs induce the S1 and S2 bands coupling with the S′ 2 and S′ 1 bands, respectively, as shown in figure 9(b). The S1 (S3) band crosses the Fermi level at 0.38 (0.62) of the YΓ length from the Γ point and at 0.37 (0.62) of the ΓM length from the Γ′ point, respectively. The constant-energy surface contours at the Fermi energy in the first SBZ, the inset of figure 9(b), show that the S′ 2, S1 and S3 bands display nearly no dispersion in the direction perpendicular to the nanowire, the 4 × direction. In fact, two upward electron-like energy troughs perpendicular to the nanowire have been formed, of which the bottom energies are about 250 meV and 350 meV below the Fermi level, separately.

Figure 9(c) shows the electronic structure of the dimer-row arrayed structure on a 0.75 ML Au/Ge(001)-c(8 × 2) surface, where the Fermi energy level shifts down ~117 meV in comparison with the 4 × 2 phase. An apparent coupling among the second layer Ge atoms below the AADRs (black solid circles) and the AGDRs (blue solid circles) exists around the Fermi level. The inset of figure 9(c) shows the constant-energy surface contours at the Fermi level, which displays the S1 and S2 bands with nearly no dispersion, and the S3 band with linear dispersion in the direction perpendicular to the nanowire. They formed as a metallic energy trough with an energy bottom of ~158 meV below EF on the YΓ line and ~113 meV below EF on the YΓ line, respectively. The energy trough feature and the band minimum are in agreement with the ARPES results taken by Schäfer et al [15] and Meyer et al [16], except the bottom energy has a small deviation; the experimental band bottom is ~130 meV below EF under resolution of ~50 meV as noted in [15]. The inset of figure 9(c) also shows that a 2D hole-like packet exists at the Y point, but it has not been found in any ARPES experiments so far; instead, another 2D hole-like packet signal was found at the half distance of the second SBZ boundary, the M point [16] (i.e. the Γ point in this work).

On the YΓ line, the linear and symmetric dispersion Dirac-like band structure presents above the Fermi level, and two small gaps were opened at the L point. This band structure is similar to the above-mentioned band structure of a c(4 × 2) phase of the 0.50 ML Au/Ge(001) surface, but the Fermi level has shifted down. The present band structure calculation is based on the GGA-PW91 scheme which tends to underestimate the gaps; thus, more elaborate methods beyond DFT-GGA (for example, DFT + U, GW, etc) should further determine the effective band gaps in this Au/Ge(001) system. Despite this, the exceptionally small band-gaps excluded the Tomonaga–Luttinger state [15] possibility according to the results of no gap opening and band back-folding suggested by the ARPES [16]. The electronic structure mentioned above is inconsistent with the other ARPES results reported at 0.96 ML Au coverage [21, 22], which presents an anisotropic 2D character metallic band with parabolic dispersion and with anisotropic effective masses from its bottom at the SBZ boundaries, which is in agreement with the results of the electronic structure calculation of the g-Ge ZC structure [28].

4. Summary and conclusion

The atomic geometry, stability, and electronic properties of Au-induced nanowires on the Ge(001) surface have been investigated as a function of Au coverage based on DFT-GGA. According to the formation energy and the STM image, the substitution of the Ge atoms by the Au atoms has been confirmed at an Au coverage lower than 0.25 ML. The simulated STM images of local single and double dimer vacancies are consistent with the experimental observations. For 0.75 ML Au coverage, the simulated STM images and the electronic band structure of the energetically favorable dimer-row arrayed atomic structures are in agreement with the shallow-groove structure of the Au/Ge(001) surface prepared at low temperatures [13, 15, 16, 20], but to form a long-range dimer-row arrayed atomic structure it must be accompanied by enough
energy to complete mass transportation of the substituted Ge atoms. In the absence of comprehensive mass transportation, the substituted Ge atoms recombine with the Au atoms and a giant deep-groove structure is prompted to form. This is why dimer-row arrayed atomic structures such as interdigitation often occur at the edges of terraces, and the ad-dimers frequently present around the single and double dimer vacancies at low Au coverage deposition [14]. Thus, the small-scale dimer-row arrayed structure as well as the majority deep-groove structure distribute over the surface so that the former structure can be regarded as a shallow-groove structure defect as per the experimental observations.

According to the quasi-1D metallic surface-state energy trough structure and the bottom energy, and the STM images, the Au exposure onto the Ge(001) surface should be close to 0.75 ML, which is in agreement with the suggestion of Meyer et al [29] and Gallagher et al [19]. Owing to the strong inter-nanowire interactions, the metallic energy troughs are formed perpendicular to the nanowire for both the 4 × 2 and c(8 × 2) phases. The electrical conductivity near the Fermi edge contributed by the shallow-groove structure is mainly from the density of states of the AGDRs and the subsurface Ge atoms below them. Specifically, it is noticed that the interesting quasi-1D electrical property displays in the 4 × 1 phase of both 0.50 and 0.75 ML Au coverages. The 4 × 1 phase structure at 0.75 ML Au coverage is also a new energetically favorable 1D electron system, which could be assembled atom-by-atom manipulation using STM or atomic force microscopy instead of self-organized formation for application.

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