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Pt-chain induced formation of Ge nanowires on the Ge(001) surface

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ABSTRACT

A new reconstructed Pt/Ge(001)–4×2 surface structure of 0.25 ML Pt deposition is suggested based on density functional theory. The Ge dimers form nanowire arrays on a Pt-chain modified Ge(001) surface in which the chain is located between the two quasi-dimer rows and below the Ge nanowire. The simulated scanning tunneling microscope (STM) images of the surface are in excellent agreement with the previously observed STM features and sample bias dependence. It is the nanowire Ge dimers and not the Pt atoms that contribute to the STM images for occupied states at high sample biases, contrary to what has always been assumed in experiments. The surface bands of the Pt chain and quasi-dimer rows exhibit quasi-one-dimensional metallic behavior in the direction of the nanowire. When changing from the 4×2 to the 4×4 structure, there are likely pseudogaps opened at the new surface Brillouin zone boundary, which simultaneously reduce the metallicity. This may be related to the Peierls instability. The interaction between the Pt chain and the quasi-dimer row, as well as the inter-quasi-dimer row interaction, is of essential importance for stabilization.

1. Introduction

Self-organized nanowire (NW) surface structures have attracted much attention among researchers. As part of the minimizing process, there is an increasing use of semiconductor nanowires [1] in nanoscale electronic and optoelectronic devices, such as field–effect transistors, sensors, detectors, and light-emitting diodes. There is also a need for ultra-thin metallic nanowires as the interconnectors among quantum devices and nanodevices in reducing the size of electronic circuits. On the other hand, ultra-thin metallic wires are important in fundamental theoretical and experimental studies because of their inherent one-dimensional (1D) exotic physical phenomena, such as the quantization of conductance, charge-density waves, Peierls instabilities, Luttinger liquid behavior and spin-charge separation [2–5]. However, only very few intriguing examples exist; sub-monolayers of Ag, Au and In atomic chains on Si surfaces are prototype examples [2,6–10]. The related papers are included in the recent review article by Snijders and Weitering [10].

Recently, noble metals deposited on Ge surfaces have attracted interest because of the observation of self-assembled nanowires on the metal/Ge surface. For instance, the deposition of sub-monolayer amounts of Pt or Au on Ge(001) induces the formation of monoatomic wires, hundreds of nanometers long [11–15]. The formation of Pt induced NWs on a Ge(001) surface was first observed by Gurlu et al. [13], and later Oncel et al. [14] and Schäfer et al. [15] succeeded in producing large arrays of very well ordered atomic chains on a Pt modified Ge(001) surface, or the so-called β-terrace. After deposition of 0.25 ML Pt on a clean Ge(001) surface, and subsequent annealing at 1050 K, self-organizing one-atom-thick, perfectly straight and defect free NWs were observed [14–17]. Both solitary wires and arrays of wires were observed, of which the latter have a constant spacing of 1.6 nm and occasionally a spacing of 2.4 nm. Based on the scanning tunneling microscope (STM) results of the Pt/Ge(001) surface [13–18], the characteristic features are as follows. (i) The NW image is dimerized. (ii) The filled state NW dimer image shows two obvious separate protrusions (double peaked for the 3D image) at high sample bias [13–18], which become less pronounced at low sample bias [17]. The empty state STM image is dominated by *single atom units* spaced about 4 Å apart when the imaging energy windows are close to the Fermi level [15], but appear as single elongated protrusions at high sample bias [17]. (iii) Almost symmetric bulges appear at both sides of the NW between the dimers [14]. (iv) Within the NW-free area, near the edges of a patch of NWs or after the top dimers have been picked up from the NW, the filled state STM image presents a widened trough between two substrate dimer rows [18]. (v) The NW dimer array images show ×2 periodicity at high temperatures, which doubles upon cooling at 4.7 K [17–19], but at the edge of a patch or isolated NW, ×2 periodicity is maintained [17]. (vi) The ×2 to ×4 periodicity transition of the NWs is accompanied by a significant reduction in metallicity [17,19]. In addition, the electronic states observed within the STM and spatial maps of the differential conductivity are interpreted as being related to Pt states or the quantization of electron states between wires [14–19]. The scanning tunneling spectroscopy results indicate the metallic conductivity of the wires at zero bias [15].

Up to now, the theoretical calculations have constructed many possible geometric structures based on density functional theory

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[20–23] to simulate the STM images for Pt deposited on a Ge(001) surface, but a number of problems remain. The tetramer–dimer-chain (TDC) model suggested by Stekolnikov et al. [21,22] and the other similar structure Ge $b(2\times1)$ T_{d1} model proposed by Vanpoucke et al. [23], which provide the best agreement with the experimental STM images to date, seemingly explain some of the observed STM features. However, the double-peak images for both positive and negative biases and the lack of symmetric bulges at both sides of the NW and between the NW dimers are in contradiction to the features of the experimental observations [20,22]. Besides, the Ge $b(2\times1)$ T_{d1} model has a positive formation energy with regard to the Ge(001) surface; this indicates that the structure is unstable compared to segregation in a Ge(001) surface and Pt bulk [20]. Thus, the Ge $b(2\times1)$ T_{d1} structure must be discarded. Nevertheless, the calculated STM images of those reconstructions show us an important result: Ge dimers could be considered as possible building blocks for the experimentally observed NWs [20,21], though this is inconsistent with the assumption of the experiments [14,15]. Vanpoucke et al. also present the calculated STM images for a Ge NW on a γ_{as}* structure, which show very good agreement with the experimentally observed NWs; however, the coverage of Pt in the Pt/Ge(001) system is at least 0.75 ML which is far greater than the 0.25 ML found in the experiments [13]. Up to the present, the theoretical models cannot completely reproduce the experimentally observed STM images. The NW formation and the bonding mechanisms are still under debate.

In this work, 0.25 ML Pt deposited on a Ge(001) surface has been studied by density-functional theory in order to reveal the atomic geometry and bonding of the resulting self-organized arrays of nanowires, and to understand their electronic structure. In Section 2, the theoretical methods used for the total energy calculations are described. By calculating the total energies and comparing the simulated with the experimental STM images, we identify the most probable structure. A novel model of Ge NW arrays above a Pt-chain modified Ge(001) structure is suggested in Section 3.1. Its simulated STM images for a wide range of sample biases are shown in Section 3.2, and are compared with the features of the experimental STM images as mentioned in the Introduction. The electronic band structure is presented in Section 3.3. This subsection also includes a discussion of the fact that when the periodicity of the NW Ge changes from $\times2$ to $\times4$, the pseudo-energy gaps open at the edges of the new surface Brillouin zone boundary and the metallicity reduces simultaneously, which may be related to the Peierls instability. Finally, the conclusions are presented in Section 4.

2. Theoretical method

The calculations of total energy were performed using VASP code [24–26] based on density functional theory (DFT) in local density approximation (LDA) and generalized gradient approximation (GGA), where the Ceperley–Alder exchange–correlation function as parameterized by Perdew and Zunger was adopted for LDA [27,28], and the Perdew–Wang (PW91) and Perdew–Burke–Ernzerhof (PBE) exchange–correlation functions were adopted for GGA [29–31]. The electronic structure calculations were specified using projector augmented wave (PAW) potentials [32], and the lower lying *d* states were treated as valence states for better accuracy. Electron orbitals were expanded by plane waves with an energy cutoff of 25.72 Ry (350 eV). For bulk Ge, the optimal lattice constant of a_0 within the LDA (GGA–PW91, GGA–PBE) is 5.62365 Å (5.75850 Å and 5.75343 Å) which is about 0.6% smaller (1.7% larger) than the experimental value, 5.6575 Å, due to the overbinding (underbinding) for LDA (GGA) treatment.

To simulate the Pt/Ge(001) surface, a repeated asymmetric slab supercell was employed. Each slab included ten Ge atomic layers with fixed bottom double Ge layers, in which Pt atoms substituted certain Ge atoms, or extra Pt atoms were adsorbed on the surface. To attain sufficiently large dimensions to prevent coupling between the slabs, the height of the supercell in the [001] direction was set to 30 Å, and the width of the vacuum region between the adjacent slabs exceeded 16 Å. In order to saturate their dangling bonds, H atoms were attached to the bottom-layer Ge atoms. The irreducible Brillouin zone was sampled with a 4×4 *k* Monkhorst and Pack mesh for a 4×4 surface unit cell. Structure optimization was performed until the residual force acting on each atom was less than 0.01 eV/Å. Constant-height mode was used to simulate the STM images according to the Tersoff–Hamann approach.

3. Results and discussion

Calculations of the total energy of more than 50 different reconstruction models have been carried out by (i) substituting 0.25 ML Ge atoms with Pt atoms on the Ge(001) surface, and by (ii) adding additional 0.25 ML Pt atoms to the Ge(001) surface. The surface formation energies of a certain geometry, *x*, with regard to the clean Ge(001) $b(2\times1)$ surface can be calculated using the expression

$$E_f = E_x - E_{Ge(001)} - \Delta N_{Pt}E_{Pt} - \Delta N_{Ge}E_{Ge}$$

with E_x the total energy of the relaxed structure, $E_{Ge(001)}$ the total energy of the Ge(001) $b(2\times1)$ surface reconstruction, E_{Pt} and E_{Ge} the bulk energy for a Pt and a Ge atom, respectively, and ΔN_{Pt} (ΔN_{Ge}) the difference in number of Pt (Ge) atoms between the relaxed structure and the Ge(001) geometry. The surface formation energies, normalized per 1×1 surface unit cell, of the proposed structure are compared with those of some of the important structures to date within LDA, GGA–PW91 and GGA–PBE, in Table 1. Because the results of GGA–PW91 and GGA–PBE are similar, in the following discussion, the data are mainly presented as LDA results, with some GGA–PW91 results shown in parentheses for comparison.

3.1. Atomic structures

From the total energy calculation results, as with the results of other calculations [20], the Pt atoms have a tendency to be incorporated into the Ge surface and to form Pt–Ge bonds which are energetically favorable to Pt–Pt and Ge–Ge [20–22]. As shown in Table 1, the formation energy per 1×1 surface unit cell of a 4×2 Pt-chain modified Ge(001) structure, referred to as the β* terrace in Table 1 and the following, is lower than that of the TDC structure by 173 meV, and that of the β terrace [33] by 228 meV within LDA. The perspective and top views of the β* terrace are shown in Fig. 1(a) and (b). The main difference in the construction of the β* terrace, the β terrace and the TDC model is that, in the β* terrace, the Pt atoms are substituted for the second layer Ge atoms of the substrate rather than for the dimer Ge atoms as they are in the latter two structures. In fact, the initial simulated geometry of the β* terrace originates from the TDC model, but in the β* terrace the Pt adatoms are exchanged with the second layer Ge atoms of the substrate. After relaxation, the Pt chain is positioned at the center of the two quasi-dimer rows and below the average top layer position at about 0.93 Å (0.97 Å), and acts as a bridge connecting the two quasi-dimer rows, QDR1 and QDR2 as indicated in Fig. 1(a) and (b). Sixfold-coordinated Pt atoms bound with the neighboring Ge atoms, four with the Ge atoms of the quasi-dimer rows, with a bond length of about 2.46–2.51 Å (2.52–2.57 Å), and two with the third layer Ge atoms, with a bond length of 2.48 Å (2.54 Å). Construction of the Pt–Ge bonds, but not the Pt–Pt bonds, is favorable for lowering the total energy; thus, this model is the most energy favorable surface structure for Pt substitution for Ge atoms in the research of 0.25 ML Pt deposited on Ge(001) to date. However, the Pt–Ge bond formation process requires large reaction energy to break the Ge–Ge bond of the substrate; consequently, the annealing temperature required for the formation should be above 1000 K, which is in accordance with the reported dimer breakup temperature of the Ge(001) surface [13,34].