Atomic Nanowires on the Pt/Ge(001) Surface: Buried Pt-Ge Versus Top Pt-Pt Chains

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Combining total-energy calculations, electronic-structure studies, and scanning tunneling microscopy (STM), we demonstrate that the observed one-dimensional nanowires are composed of Pt-induced Ge structures instead of Pt chains. Pt-Ge bonds are favored versus Pt-Pt ones. The novel tetramer-dimer-chain model explains STM features and the differential conductivity. The conduction path is related to the chain of alternating Pt-Ge atoms.

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Self-organized quasi-one-dimensional surface structures have attracted enormous attention. Besides possible future applications, the interest is driven by a wealth of novel exotic physical phenomena predicted for one-dimensional (1D) systems. A key feature is the possibility of a Peierls instability, leading to formation of a charge density wave (CDW). In addition, one should observe Luttinger liquid behavior and spin-charge separation.

Nanowires on semiconductor surfaces have attracted special interest because of their narrow width of a few atoms, thereby forming model systems for the study of 1D physics. While the 5*d* noble metals Ir, Pt, and Au tend to form surface reconstructions containing chains on their own low-index surfaces [1], metallic chains were also observed on Ge and Si(001) substrates after Pt or Au deposition [2–5]. However, the chain formation and the bonding mechanism are still under debate. In particular, the role of the 5*d* states for the coordination of the metal atoms is controversially discussed. This also holds for the question why 4*d* metals such as Pd do not give rise to ordered metallic chains [6]. The common picture is that the strong relativistic character of the 5*d* states leads to the preference for low coordination of Au, Pt, and Ir atoms and hence the formation of dimerized chains, instead of cluster formation [1,4–6].

The Pt-induced 1D structures on Ge(001) lend themselves to the study of the interplay of Pt-Pt, Pt-Ge, and Ge-Ge bonds in the self-organization of chains. After room temperature (RT) deposition of about 0.25 monolayer (ML) of platinum, annealing leads to the formation of wires with extremely high aspect ratios [3,5,7]. The top atomic chains seemingly exhibit dimerization which becomes small for tunnel bias close to the Fermi level [8]. The electronic states observed within scanning tunneling microscopy (STM) are interpreted to be related to Pt states [2,5,7,8] or quantization of electron states between wires [5,9]. The scanning tunneling spectroscopy (STS) results indicate a metallic conductivity of the wires at zero bias [2,8].

In this Letter, we report on theoretical and experimental studies of the Pt adsorption on Ge(001) surface in order to reveal the atomic geometry and bonding of the resulting self-organized array of nanowires and to understand their electronic structure. The analysis of numerous structural models favors a novel reconstruction with Pt-Ge bonds instead of Pt-Pt bonds which explains the STM images. While Ge dimers reside on top of the chain, the Pt atoms are located to the side of the ridge.

The theoretical studies are based on density functional theory (DFT) in generalized gradient approximation (GGA) as implemented in the VASP code [10]. The pseudopotentials have been generated within the projector augmented wave (PAW) scheme. According to the STM studies [2,5,8], usually a 4×2 translational symmetry with rectangular unit cells is used. A number of 32 *k*-points of Monkhorst-Pack type is taken in the irreducible part of the Brillouin zone (BZ). Constant-height mode is used in order to simulate STM images within the Tersoff-Hamann approach.

Experimentally, Ge(001) substrates were prepared by repeated cycles of Ar sputtering and annealing to 800 °C. The sample received a post-deposition anneal at 600 °C to allow formation of the well-ordered nanowire reconstruction. STM measurements were performed under ultrahigh vacuum conditions at RT (for details see [8]). As an example, an occupied-state image of a Pt/Ge(001) surface with self-organized nanowires in a distance of 16 Å in [110] direction and a periodicity of 8 Å in $[1\bar{1}0]$ direction is shown in Fig. 1(a).

The translational symmetry corresponds nominally to eight Ge atoms in one (001) atomic layer of the substrate. In the case of the clean Ge surface, one cell would contain two rows of Ge dimers in [110] direction with a total of four dimers. We have studied more than 20 different reconstruction models by means of total-energy calculations. The assumption of 0.25-ML coverage follows experimental results in Refs. [5,7]. In addition, our desorption studies indicate that the nanowire phase corresponds to the lowest

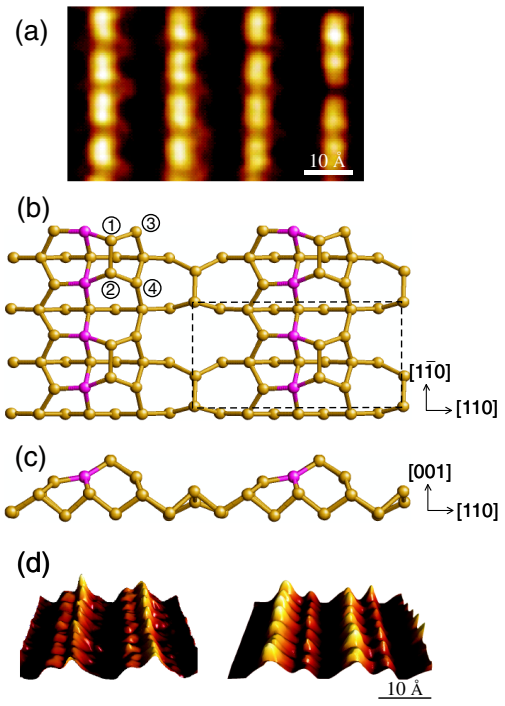

FIG. 1 (color online). (a) STM image (61 Å × 33 Å) of a self-organized nanowire array on a Pt/Ge(001) surface showing occupied states at −1.35 V. Top (b) and side (c) view of the tetramer-dimer-chain model of the 0.25 monolayer Pt/Ge(001)4 × 2 surface. In the stick-and-ball model, the dark circles represent Pt atoms. A possible 4 × 2 surface unit cell is indicated by dotted lines. (d) STM images of identically oriented nanowire arrays of the very same sample at +1.70 V, revealing the existence of domains with left and right asymmetry.

possible coverage. As a consequence of two Pt atoms per 4 × 2 unit cell, first, we followed the idea of a formation of symmetric Pt-Pt homodimers [7–9] or Pt-Ge heterodimers arranged in chains on top of the Ge surface. Dimerized Pt chains are formed by breaking the π bonds of substrate dimers. Thereby, the Pt atoms bridge four or two Ge dimers parallel to the rows. Indeed, these structures give rise to local minima on the total-energy surface. They also show strong bonds between Pt and Ge. Refinements as the formation of five or sevenfold rings similar to the Bi/Si(001) system [11,12] do not improve the stabilization of the suggested surface structures. However, the total energy can drastically be reduced by avoiding Pt-Pt bonds. Fourfold-coordinated Pt atoms with Ge neighbors turn out to be very stable reconstruction elements.

In the next step, we have combined the idea of fourfold-coordinated Pt atoms arranged in linear chains with that of the formation of Ge tetramers [13]. We obtained a surface reconstruction which is slightly asymmetric as shown in Figs. 1(b) and 1(c). Compared with the above discussed models, this new reconstruction reaches the global minimum on the total-energy surface. The resulting tetramer-dimer-chain (TDC) model yields a substantial energy gain in the grandcanonical thermodynamical potential of about 2 eV per 4 × 2 unit cell with respect to the reconstructions with top Pt dimers or 80–150 meV per 4 × 2 unit cell with respect to the reconstructions with heterodimers and Pt in the second layer.

The incorporated Pt atoms give rise to alternating rows of twofold-coordinated (001)-like top Ge atoms with two dangling bonds and threefold-coordinated (111)-like Ge atoms below with one dangling bond. The pairing, even without dimerization, of two topmost (001)-like atoms along the [110] direction [atoms 1 and 2 in Fig. 1(b)] leads to a ×2 reconstruction. Together with two (111)-like atoms in almost [1$\bar{1}$ $\bar{1}$] direction [atoms 3 and 4 in Fig. 1(b)] the four atoms form a Ge tetramer or, if one additionally counts the connected atom in the third atomic layer, a pentamer. This structural element has been found to stabilize Ge(113) surfaces and tends to open a gap (see Ref. [13] and references therein). Together with the Ge dimers in the trenches parallel to [1$\bar{1}$0], a 4× reconstruction appears in [110] direction. There are three main arguments for the energy lowering compared to a model with top chains of Pt-Pt homodimers: (i) One more Pt-Ge bond and replacement of a Pt-Pt by a Pt-Ge bond per Pt atom, (ii) Ge tetramer formation which usually makes a (113) surface of group-IV semiconductors to the second most stable face, and (iii) electron transfer from adjacent Ge dangling bonds into Ge-Pt bonds close to the Pt atoms.

The resulting nanowires possess a complex bonding geometry. The topmost Ge atoms form linear ridges of dimerlike pairs. The Pt atoms give rise to evenly spaced linear chains without Pt-Pt bonds. In [1$\bar{1}$0] direction, they are accompanied by parallel zigzag chains of rebonded Ge atoms with one remaining dangling bond. The Pt chains on one side of the topmost Ge chains and the tetramers on the other side explain the subtle asymmetry perpendicular to the nanowires observed in the STM images. Notably, the top ridge of the chain reconstruction is formed by Ge-Ge dimers, standing up high above the surface [see Fig. 1(c)], while the Pt atoms are located below. This will lead to seemingly almost symmetric dimerlike features in experimental STM overview images, especially since the Ge-Ge top dimers are strongly contributing to constant-current images discussed below.

The proposal of an asymmetric reconstruction on a formerly symmetric substrate surface is also substantiated by the observation of phase and antiphase reconstructions in the experiment. Figure 1(d) shows STM data from two terraces with identical orientation of the underlying Ge substrate dimer rows. The two nanowire arrays, on the same sample, are oriented in antiphase to each other, compatible with our model. Asymmetric structural units have also been observed in other high-resolution measurements [2,8].

The characteristic edge lengths of the rectangular unit cell are $2\sqrt{2}a_0 \approx 16$ Å and $\sqrt{2}a_0 \approx 8$ Å with a cubic substrate lattice constant of about 5.65 Å but increased in the computations by more than 1%. The vertical distance

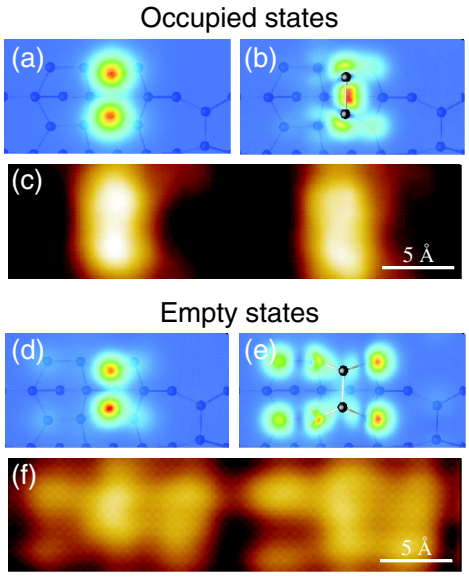

FIG. 2 (color online). STM images simulated for the TDC model in one 4×2 unit cell (see Fig. 1) for two bias voltages -1 V [occupied states, panels (a), (b)] and $+1$ V [empty states, panels (d), (e)]. The calculated constant-height images are plotted for a plane 3 Å above the topmost Ge atoms [(a), (d)] and within these atoms [(b), (e)]. The experimental images taken at -1.35 V (c) or 1.35 V (f) are presented in two unit cells.

between the trench Ge dimers and the top Ge pairs amounts to about 4 Å. The Ge pairs in the top chain exhibit only a vanishing buckling. The same holds for the puckering tendency of the tetramer. However, the Ge dimers in the trenches between two wires [Figs. 1(b) and 1(c)] show a remarkable buckling amplitude of about $\Delta z = 0.83$ Å. This dimer buckling indicates a possible transformation into a $\times 4$ reconstruction. A doubling of the unit cell to a $8\times$ reconstruction in the perpendicular direction would be easily possible by an antiphase arrangement of the neighboring chains similar to the case of the In/Si(111)8×2 surface [14]. But such unit cell doubling alignment has not yet been observed for the Pt/Ge system. The increase of the chain distances from $2\sqrt{2}a_0$ to $3\sqrt{2}a_0 \approx 24$ Å (and consequently a 6×2 reconstruction) by a missing row defect, as observed [8,9], is also possible by extending the trench region within the above described TDC model.

How the atomic geometry is reflected in the electronic structure is demonstrated by the simulated STM images in Fig. 2. For the tip above the topmost surface layer, one only observes image maxima due to more or less symmetric Ge pairs. Their σ bonds are clearly visible in the occupied-state image [Fig. 2(a)] while the empty-state image [Fig. 2(d)] is dominated by the corresponding antibonding states as well as empty π orbitals. Moving the plane down (constant-height mode), still the σ bond is visible [Fig. 2(b)]. However, in addition, bonding states with the Pt atoms (left) and the Ge tetramer (right) are partly visible indicating the asymmetry of the nanowire structure. The combination of these phenomena, including pairing and asymmetry, is consistent with the experimental STM image in Fig. 2(c). The small difference of the bias voltage in calculated and measured images has been chosen to account for quasiparticle shifts missing in the DFT-GGA. Moving the plane down the theoretical empty-state image in Fig. 2(e) becomes much more complex in agreement with the experimental one in Fig. 2(f). In particular, in both theoretical and experimental images, six protrusions occur to characterize one chain segment. Away from the topmost Ge pairs, the empty Gep_z-type dangling bonds of the two other tetramer atoms can be seen on the right. Protrusions on the left belong to empty dangling bonds of strong Ge sp^3 or Pt d_{xy} character. Altogether, the TDC model represented in Fig. 1 is indeed able to explain also the much more complex and asymmetric empty-state images without taking into account Pt-Pt bonds.

The comparison of the STM images in Fig. 2 sustains the suggestion that all Pt atoms are fourfold coordinated by Ge atoms. The Pt $5d$ states play a substantial role in the bonding. In addition, the bonding is influenced by a charge transfer into Pt $6s$ states. The left Ge neighbors donate an electron towards the central Pt atom. Moreover, an electron promotion of d into s states occurs. The TDC reconstruction model supports the idea that the adsorption of noble $5d$ atoms tends to strong, more directional bonds including the $5d$ states with substrate atoms. This seemingly also holds in the case of metal substrates on which $5d$ elements form chains of atoms [1,15]. This tendency seems to be enforced for covalent group-IV substrates as also demonstrated for Au on Ge(001) [4,6]. Moreover, the incorporation of Pt and Au atoms in the group-IV material for not too high coverage gives the same coordination as for such $5d$-atom impurities at substitutional sites in bulk.

The direct and indirect involvement of $5d$ states can be made obvious studying the electronic structure of the self-organized nanowire arrays in more detail. According to the electronic structure calculations, Pt d states occur near the Fermi level together with Ge states localized at the top pair of the tetramer. In Fig. 3, we have plotted the calculated

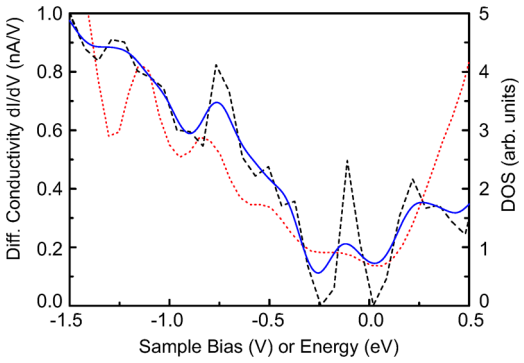

FIG. 3 (color online). Calculated density of states for the Pt/Ge(001) system using the TDC model together with measured differential conductivity (dotted line) averaged over the nanowire region. The theoretical spectra are broadened by parameters 10 meV (dashed line) and 100 meV (solid line).

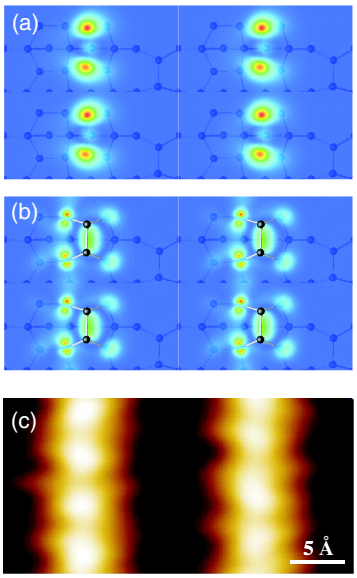

FIG. 4 (color online). Low-bias STM images from simulation (a), (b) and experiment (c) demonstrating the emergence of monomers (four unit cells are shown). The integrated local density of states has been calculated for an energy −0.1 eV below the Fermi energy, while the experimental one has been taken for a bias of −0.25 eV. The constant height images are plotted for a plane 3 Å above the topmost Ge atoms (a) and just below these atoms (b).

density of states (DOS) around the Fermi level E_f as energy zero together with the differential conductivity dI/dV averaged over the nanowire. In addition to a theoretical curve for a small broadening, another one is presented for a larger broadening in order to simulate the temperature influence and to compare with measured RT data. A small shift in the peak positions may be attributed to the doping level of the measured samples. The figure shows a nice agreement of theory and experiment around the Fermi level or zero bias and in the occupied DOS region. There is a clear indication for a finite conductivity at RT while for low temperature (theoretical curve for small broadening), one observes a tendency for zero density at E_f. Actually, the DFT-GGA band structure shows a zero gap with band extrema near J and K in the BZ. Band dispersion around E_f occurs virtually only in chain direction, consistent with the 1D appearance of the STM images. Near energies of −0.25 eV, a small gap appears between occupied states. These observations are in close agreement with the low-temperature studies of Oncel *et al.* [5] and the experimental RT curve in Fig. 3. The DOS peak between the two gaps is mainly due to bonding combinations of Pt d and Ge sp^3 states. The onset of the DOS above the Fermi energy is also related to Pt d states. However, with increasing energy, empty dangling bond states localized at the Ge atoms between trench dimers and Pt chains mix in.

The pronounced peak in the DOS (Fig. 3) just below the Fermi level leads to the expectation of interesting electronic properties for small bias voltages of 250 meV. Indeed, they are demonstrated in Fig. 4 by both theoretical and experimental occupied-state images. In contrast to high-bias images in Fig. 2, at lower bias, the pairing effect in the top Ge chains due to the tetramer formation is no longer visible or at least largely suppressed. The accompanying monomer character can easily be seen in the simulated [Fig. 4(a)] and measured [Fig. 4(c)] images. This phenomenon is dominated by Ge sp^3-like states localized at the top Ge chain atoms. The strongly directional behavior of these states is the reason why the spot maxima occur at a distance larger than the upper edge length of the tetramers and slightly displaced perpendicular to the wire direction away from the top Ge chain. Taking a lower plane (at 2 Å below top atoms) for the simulated images [Fig. 4(b)], one observes a strong contribution of Pt states.

In summary, using *ab initio* calculations and STM measurements, we have studied quasi-one-dimensional nanowire arrays induced by low-coverage Pt adsorption on the Ge(001) surface. The tetramer-dimer-chain model was found to describe the most stable surface reconstruction. It is mainly characterized by top chains of Ge pairs which are connected to fourfold-coordinated Pt atoms on one side and Ge tetramer atoms on the other side. Experimental and theoretical data agree well for STM images and the density of states. We have shown that the observed characteristic maxima in occupied-state STM mainly originate from Ge atoms. Near the Fermi energy, Pt-derived electronic states play an important role in addition.

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