Formation of atomic Pt chains on Ge(001) studied by scanning tunneling microscopy

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Recently, it was found that atomic Pt chains can be grown on Ge(001) surfaces. These kink-free wires only grow on specific Pt-modified, so-called β terraces, which are one atom wide and up to a micron long. Their self-assembly includes a crucial, high-temperature annealing step, following low-temperature (sub-) monolayer deposition. So far, details of the formation process remained unclarified. Here, we report on the formation of the Pt atomic chains on the Ge(001) surface after a high-temperature annealing at 1100 K. The results suggest that at high temperature, the platinum, previously submerged during and after deposition, emerges and forms Pt dimers located in the troughs between the surface dimer rows, which locally widen in this process. These Pt dimers are initially oriented parallel to the substrate dimers. However, upon surpassing a critical local coverage, the Pt dimers rotate by 90°, resulting in a zipperlike formation of the Pt chains.

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The physical properties of a system depend strongly on its dimensionality. One-dimensional electron systems are especially interesting because they exhibit a wealth of exotic physical phenomena, such as the quantization of conductance, Peierls instability, and Luttinger liquid behavior.[1–9] Besides this fundamental interest, one-dimensional systems are also important from a technological point of view. For instance, semiconductor nanowires are increasingly used in electronic devices, including field-effect transistors, sensors, detectors, and light-emitting diodes.[10–14] Metallic nanowires can also be utilized as interconnects for quantum devices and nanodevices.[15,16]

An attractive route to grow nanowires is by depositing metal atoms on a vicinal surface. The temperature is chosen such that the metal atoms can reach the preexisting step edges. Vicinal Si surfaces are often used as a template for nanowire growth.[17,18] A notorious problem of these surfaces, however, is the presence of thermally excited kinks in the steps, eventually leading to disordered nanowires.[19]

Recently, we succeeded in producing large arrays of Pt chains on a semiconductor surface.[20] Using a similar procedure, monoatomic wires are found for the Au/Ge(001) (Refs. 21 and 22) and Au/Si(001) (Ref. 23) systems, while the deposition of Pd or Ag on Ge(001) favors the formation of three-dimensional clusters.[24,25] The self-organizing Pt chains have a cross section of only one atom, are perfectly straight, and are defect free. For these reasons, these Pt chains can be considered as ultimate nanowires. Though the physical properties of these Pt chains become gradually unveiled,[26] the formation process of these atomic Pt chains has remained unclarified.

Here, we focus on the formation process of these Pt nanowires in a detailed scanning tunneling microscopy (STM) study. Although high-temperature measurements with STM are, in principle, possible, the study of the formation of the Pt atomic chains near the melting temperature is complicated by the low diffusion barrier of Ge adatoms and ad-dimers. At elevated temperatures, the diffusing Ge dimers will hamper atomic resolution. However, *a posteriori* inspection following a quick freeze-in, at different stages of the formation process, provides relevant insight into the formation process. Our measurements reveal that Pt atoms deposited at room temperature initially intermix with the bulk, but upon a high-temperature annealing treatment, they pop up from the bulk as Pt dimers. Initially, these Pt dimers are located in between the substrate dimer rows and are oriented parallel to the substrate dimers. Upon reaching a critical coverage, the Pt dimers spontaneously rotate by 90° and form an atomic Pt chain in between the substrate dimer rows.

Experiments were performed with an Omicron low-temperature STM operating in ultrahigh vacuum. Ge(001) substrates were cut from nominally flat 3 in.$\times$0.5 mm, about 25 Ω cm resistance, single-side-polished *n*-type wafers. Samples were mounted on Mo holders, and contact of the samples to any other metal during preparation and experiment has been carefully avoided. The Ge(001) samples were cleaned by prolonged 800 eV Ar^+ ion sputtering and annealing via resistive heating at 1100 (±25) K. The temperature is measured with a pyrometer. After several cleaning cycles, the Ge(001) samples were atomically clean and exhibited a well-ordered $(2\times1)/c(4\times2)$ domain pattern, as can be seen in Fig. 1.[27] Subsequently, an equivalent of 0.20–0.30 monolayers of platinum was deposited onto the surface at room temperature. Platinum was evaporated by resistively heating a W wire wrapped with high purity Pt (99.995%). After Pt deposition, the sample was annealed at 1050 (±25) K, and then cooled down to room temperature by radiation quenching before placing it into the STM for observation.

After the deposition of Pt on Ge(001) and subsequent annealing at temperatures above 1050 K, two different types of terraces are formed on the Ge(001) surface, denoted as α and β terraces.[20] Figure 1(a) shows an STM image of a clean dimer reconstructed Ge(001) surface. The dimer rows in the $c(4\times2)$ domains have a zigzag appearance as they are comprised of buckled dimers. The other dimer rows have a symmetric appearance and consist of dimers that rapidly flip-flop between their two buckled configurations.[28] An STM image of an α terrace is displayed in Fig. 1(b). The α terraces are comprised of symmetric and asymmetric Ge dimers and re-

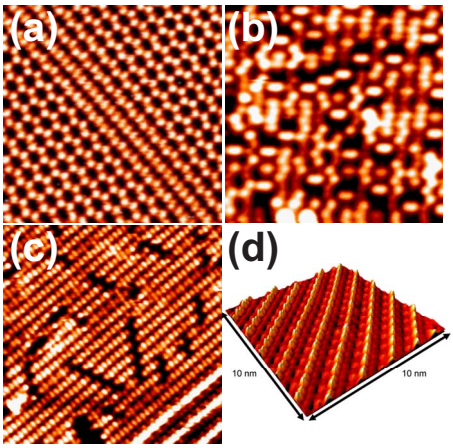

FIG. 1. (Color online) (a) STM image (10×10 nm^2, bias voltage of −1.5 V, tunneling current of 0.4 nA) of the cleaned Ge(001) surface prior to Pt deposition. The dimer rows that have a zigzag appearance show the $c(4\times2)$ reconstruction. Within the center of the image dimer, rows exhibit the (2×1) reconstruction. (b) STM image (10×10 nm^2, bias voltage of −1.0 V, tunneling current of 0.4 nA) of an α terrace after Pt deposition on the Ge(001) surface and subsequent annealing steps. Note the high amount of defects. (c) STM image (15×15 nm^2, bias voltage of −0.3 V, tunneling current of 0.5 nA) of a β terrace after Pt deposition on the Ge(001) surface and subsequent annealing steps. Note the vacancy clusters aligned in the ⟨310⟩ and ⟨110⟩ directions. In the bottom right corner, a few Pt atomic chains are found. (d) STM image (10×10 nm^2, bias voltage of −0.1 V, tunneling current of 0.2 nA) of a β terrace covered with atomic Pt chains. The interchain distance is 1.6 nm. The chains are comprised of dimers.

semble the normal dimer reconstructed Ge(001) terraces rather well.[29] The amount of missing dimer defects and adatoms is, however, much higher as compared to the bare Ge(001) surface. Most of these missing dimer defects can be identified as 2+1 missing dimer defects (two missing dimer defects followed by a normal dimer and a missing dimer defect). It is believed that these defects are induced by the presence of a metal atom, such as Ni, Ag, Cu, Co, or, in our case, Pt atom, sitting in a subsurface position.[30] Figure 1(c) shows an STM image of a β terrace. The surface is again dimer terminated, but in this case the termination consists of an ordered array of dimers that clearly deviate from normal Ge-Ge dimers, as they are apparently Pt modified.[20] Another remarkable feature of these β terraces is the presence of dimer vacancy lines, which are always aligned along the ⟨310⟩ and ⟨110⟩ directions. These vacancy lines are unknown to the bare Ge(001) surface and the α terraces. Interestingly, patches of atomic Pt chains are exclusively observed on the β terraces. An STM image of such a patch of atomic Pt chains is shown in Fig. 1(d). The chains have a cross section of one atom, are kinkless, and are defect free. The atomic chains are located in troughs between the substrate dimer rows. The interchain distance is found to be mostly 1.6 nm, although spacings of 2.4 nm and sometimes even of 3.2 nm, 4.0 nm, etc., are found as well. The majority of the atomic chains are found in patches. Occasionally, isolated Pt chains are also observed. It should be pointed out that adjacent Pt dimers in neighboring rows are in registry with each other for a separation of 1.6 nm and out of registry for a separation of 2.4 nm.

The high-temperature (i.e., annealing at ~1050 K) treatment turns out to be essential for the formation of the Pt chains. In order to obtain more detailed insight in the nanowire formation mechanism, we have used here an annealing time of 1 s in contrast to our previous work, where we used an annealing time of about 10 min.[20] As a matter of fact, independent of the actual duration of annealing at 1050 K, we have always observed the formation of atomic Pt chains. Figure 2(a) shows an STM image of the Pt chain covered Ge(001) surface after high-temperature annealing at 1050 K for 1 s. Large fractions of the surface are covered with Pt chains running along the substrate dimer row directions. In the center of Fig. 2(a), a narrow Pt-chain-free area is observed. Whitin this chain-free region, the trough between two substrate dimer rows widens. The widening starts from two ordinary substrate dimer rows in the upper right corner of Fig. 2(a). This widening process resembles the behavior of a zipper rather well. In the widened trough, two isolated and one cluster of two elongated features are visible. The elongation direction is along the substrate dimer bond direction. These widened troughs are often found near the edges of a patch of Pt chains [Figs. 2(c) and 2(d)].

We suggest that the protrusions in this widened trough are comprised of Pt dimers that are aligned along the substrate dimer bond direction. The Pt chain eventually forms because these Pt dimers rotate by 90°, leading to a Pt chain in the trough between the substrate rows. This rotation process is quite similar to the rotation of a Si dimer on top of the substrate dimer rows of a Si(001) surface.[31] The ad-dimer axis is initially perpendicular to the substrate dimer row direction, and it rotates to a parallel configuration. However, the Pt rotation process takes place in between the substrate dimer rows rather than on top of the substrate dimer rows.

In Fig. 2(b), a broad trough is shown that contains a fragment of a well-ordered Pt chain in the trough as well as several Pt dimers in the "wrong" orientation. The Pt dimers in these widened trough positions are found in singles or in pairs [see Fig. 2(b)]. In our experiments, the vast majority of Pt dimer clusters consist of one or two Pt dimers in the wrong orientation. This suggests that the Pt dimers rotate by 90° and form a chain as soon as the Pt dimer cluster becomes larger than two dimers. The amount of Pt dimers we have observed varies from troughs that contain only a few Pt dimers [Fig. 2(a)] up to troughs that contain about half the number of misaligned Pt dimers needed for a complete Pt chain [see Figs. 2(c) and 2(d)].

Using the STM tip as a nanotweezer, we were able to pick up Pt dimers from the Pt chain. Figure 3 shows an STM image of a region covered with several Pt chains (left hand side). In the right hand side, several Pt dimers have been removed from the second Pt chain by the STM tip.[32] Under the Pt chain, we see again the widened trough. Thus, widened trough remains intact after the rotation of the Pt dimers from the wrong orientation to the "right" orientation.

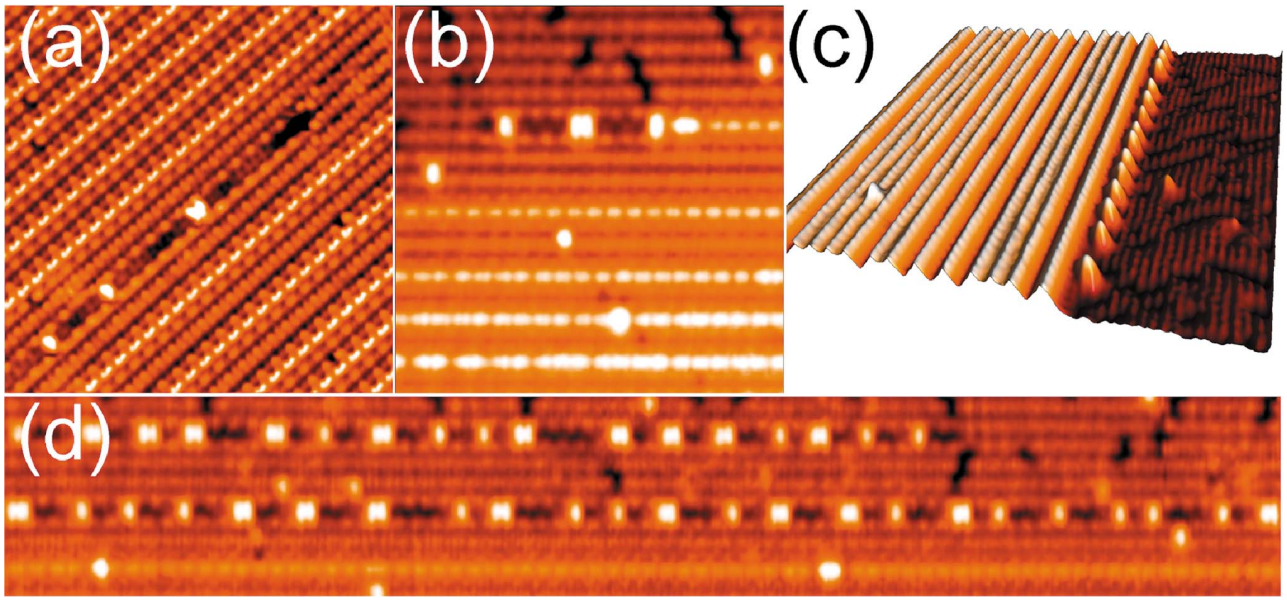

FIG. 2. (Color online) (a) STM image of the Pt-modified Ge(001) surface after a 1 s high-temperature annealing at 1050 K. The image size is 15×15 nm^2. The bias voltage is −0.50 V with a tunneling current of 0.5 nA. (b) The STM image of the Pt-modified Ge(001) surface after a 1 s high-temperature annealing. The image size is 14×14 nm^2. The bias voltage is −1.2 V with a tunneling current of 0.4 nA. (c) Three-dimensional STM image of the Pt-modified Ge(001) surface after a high-temperature annealing. The image size is 37.5×37.5 nm^2. The bias voltage is 1.50 V with a tunneling current of 0.2 nA. (d) Two-dimensional STM image of the Pt-modified Ge(001) surface after a high-temperature annealing. The image size is 10×50 nm^2. The bias voltage is −1.45 V with a tunneling current of 0.4 nA.

In our experiments (after 1 s annealing at 1050 K), the Pt dimers in the widened trough positions are found in singles or in pairs [see Fig. 2(b)]. In previous work, we used an annealing time of 10 min.[20] An STM image of a prolonged annealed (10 min). Pt-modified Ge(001) surface is shown in Fig. 4. A variety of interesting features can be observed. Firstly, it reveals that once the chains have nucleated, the chains expand easily along the dimer row direction. As a consequence, the Pt chains are as long as possible; i.e., their length is only limited by defects in the terrace, preexisting step edges, or out-of-registry neighboring chains. The latter acts as an antiphase boundary (denoted by 1 in Fig. 4). Antiphase boundaries also occur in the direction perpendicular to the Pt chains, as a result of the coalescence of neighboring chain patches. In this case, the antiphase boundary consists of a 2.4 nm wide trough between the neighboring Pt chain (denoted by 2 in Fig. 4). In Fig. 2(c), it can be seen that the nucleation of a new Pt chain occurs preferably at the edge of a patch with an interchain distance of 1.6 nm. This explains the formation of large patches of Pt chains (see Fig. 4). Besides these patches, quite a number of isolated atomic Pt chains are also formed. The majority of these isolated Pt chains consist of Pt dimers in a wrong orientation; i.e., these Pt dimers have their dimer bond aligned in a direction perpendicular to the trough. Obviously, these unrotated Pt dimer line segments are relatively stable. In addition, a more careful analysis of the these line segments reveals that the number of unrotated Pt dimes that is required to form a well-oriented Pt chain in the trough is too high. However, it remains unclear why this occurs mainly for the isolated atomic Pt chains. We believe that the rotation process of the Pt dimers in the unrotated dimer line segments is sterically hindered. The latter leads to Pt chains with thick "tails" of Pt dimers in the wrong orientation (denoted by 3 in Fig. 4). Additionally, double step edges on α terraces are found occasionally to be decorated with a row of Pt atoms (denoted by 4 in Fig. 4).

In order to elucidate the kinetic and energetic details of the formation process of the Pt atomic chains, an *in situ* observation using a high-temperature STM would be very valuable.

In summary, we studied the formation of well defined, defect and kink-free Pt atomic chains on a Pt-modified

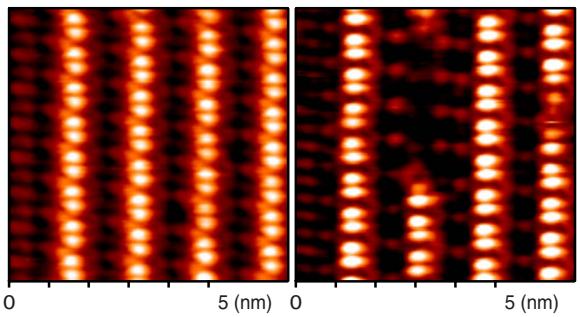

FIG. 3. (Color online) STM images (7.0×7.0 nm^2, bias voltage of −0.020 V, tunneling current of 0.5 nA) of a region covered with Pt chains. Before manipulation experiment (left hand side) and after the removal of some Pt dimers from the second Pt chain (right hand side). Note the structure of the underlying (widened) trough.

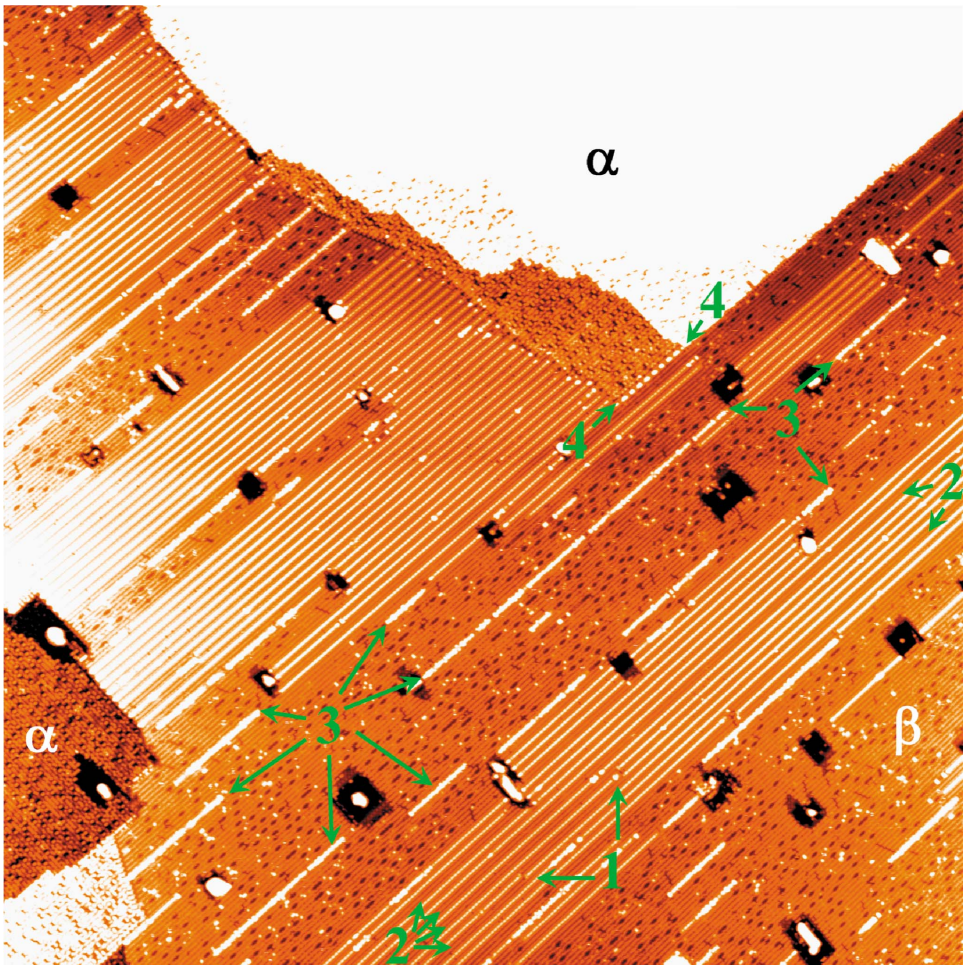

FIG. 4. (Color online) STM image (150×150 nm^2, bias voltage of -1.5 V, tunneling current of 0.4 nA) of a prolonged annealed Pt-modified Ge(001) surface. α and β terraces are indicated. On the β terraces, atomic Pt chains at varying lengths are visible. Antiphase boundaries along and perpendicular to the Pt chain direction are respectively indicated with 1 and 2. Pt chains contained in the wrong rotation, which are sterically hindered in the rotational motion, are labeled with 3. The number 4 marks a double step on an α terrace decorated with Pt atoms.

Ge(001) surface with STM. Initially, the Pt atoms deposited at room temperature submerge the subsurface. After annealing at elevated temperatures, the surface opens locally in a zipperlike manner and the Pt atoms emerge as pairs within the widened trough between the two substrate dimer rows on the β terraces. Finally, this is followed by a 90° rotation of the Pt dimers, giving rise to well defined atomic Pt chains. However, an *in situ* observation of the Pt atomic chain formation using a high-temperature STM is needed to elucidate the kinetics of the chain formation process.

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