Surface Science Letters

One-dimensional Gd-induced chain structures on Si(1 1 1) surfaces

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Abstract

A one-dimensional 5×2 reconstruction of Gd is observed on Si(1 1 1), which can be stabilized in single domain form on vicinal surfaces. It contains zig-zag rows of occupied orbitals alternating with rows of unoccupied orbitals, as inferred from spectroscopic scanning tunneling microscopy. The large magnetic moment of the Gd 4f electrons creates atomic chains with a magnetic coupling. © 2001 Published by Elsevier Science B.V.

The electronic structure undergoes a dramatic change when the geometry restricts electrons to two dimensions. Extensive experimental studies have been dedicated to explore the resulting quantization phenomena in layered structures, such as quantum well states and the quantum Hall effect. Studies of one-dimensional systems are found less often, despite predictions of exotic behavior, such as the separation of the spin and charge of electrons. The problem is producing a sufficient quantity of one-dimensional wires and aligning them all in the same direction, such that they can be studied by macroscopic methods. Using a surface science approach, one can start with a two-dimensional layer and confine the electrons further to one dimension. Chain-like reconstructions of metals on semiconductor surfaces provide a natural vehicle to explore one-dimensional electrons, provided that the electronic states of adjacent chains are sufficiently decoupled from each other and from the bulk states of the substrate. That can be achieved by sufficient chain separation and by having metallic states at the Fermi level that lie inside the gap of the semiconductor substrate. Examples of such structures are Si(1 1 1)4 × 1–In [1], Si(1 1 1)5 × 2–Au [2–6], and Si(5 5 7)–Au [6–9]. They exhibit special electronic features, such as a Peierls transition [1], a band with variable dimensionality [5], and two nearly degenerate bands [8,9]. The last one has been attributed to spin

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charge separation [8] or to a bonding/antibonding splitting in the unit cell [9]. The theoretical phase diagram of one-dimensional phases contains charge density waves, spin density waves, superconductivity, the Luttinger liquid [10], the Luther–Emery liquid [11], and other exotic states. For a controlled synthesis of these phases it is important to control the coupling parameters that govern the phase diagram, such as the band filling, the intra-chain and inter-chain hopping T, the on-site Coulomb repulsion U, and the magnetic coupling J. Here we address the possibility of introducing a magnetic coupling via incorporating magnetic atoms into a one-dimensional chain reconstruction.

We report a one dimensional 5×2 structure of Gd on Si(1 1 1), which spontaneously breaks the threefold symmetry of the surface. A single domain is stabilized on a vicinal surface. Gadolinium is particularly useful for generating magnetic interactions because of its high magnetic moment. There are seven electrons in the half-filled 4f shell, which are spin-aligned according to Hund's first rule. Coupling of these moments via direct exchange or via the conduction electrons along an atomic chain should provide interesting magnetic interactions in one-dimension. Using scanning tunneling microscopy (STM) with spectroscopic imaging we find a maximum separation between rows of occupied and unoccupied orbitals, indicating ionic character.

For the preparation of a single-domain Si(1 1 1)-5×2–Gd surface we used vicinal Si(1 1 1) with a miscut of 1° towards the [$\bar{1}\,\bar{1}\,2$] azimuth. A regular pattern of straight steps can be achieved with this miscut [12], which aligns all 5×2 domains parallel to the steps. About 0.3 monolayer of Gd was deposited from a miniature electron-beam evaporator with a flux of 0.002 monolayer/s. The sample was held at a temperature of 700 °C during evaporation. The exact amount of Gd at the surface is difficult to determine accurately due to the fact that Gd diffuses into the bulk above 600 °C and segregates back to the surface during cooling. After repeated cycles of Gd deposition and flash cleaning at 1250 °C it was possible to convert Si(1 1 1)7×7 into Si(1 1 1)5×2–Gd by just annealing the sample to 600 °C, the necessary Gd being supplied by outdiffusion from the bulk. Our best estimate of the coverage is consistent with 0.2–0.4 monolayers, i.e.,

1–2 Gd chains per unit cell. For comparison, the Si(1 1 1)5×2–Au structure has a coverage of 0.44 monolayers of gold [2]. At higher coverage a $\sqrt{3} \times \sqrt{3}$-Gd structure is formed, analogous to the situation with Au. The Si(1 1 1)5×2–Gd surface is highly reactive, with a lifetime of a few hours in a vacuum of $<1 \times 10^{-10}$ Torr, compared to days for Si(1 1 1)5×2–Au. Adsorbed residual gas atoms may appear as bright protrusions or dark depressions in the STM images (see inset in Fig. 1).

The STM images of the Si(1 1 1)5×2–Gd surface in Fig. 1 show long, parallel chains that are resolved into individual rows of atoms in the inset. The full panel depicts the x-derivative of the topography, which is also used for Figs. 2 and 3. Thereby, the surface appears to be illuminated from the left with the steps casting dark shadows to the right, which is downhill. The inset shows the topography itself. The steps are one to three Si double layers high. The close-up image of the chains in the inset of Fig. 1 reveals a 5×2 reconstruction, which is confirmed by low-energy electron diffraction. Each chain consists of two
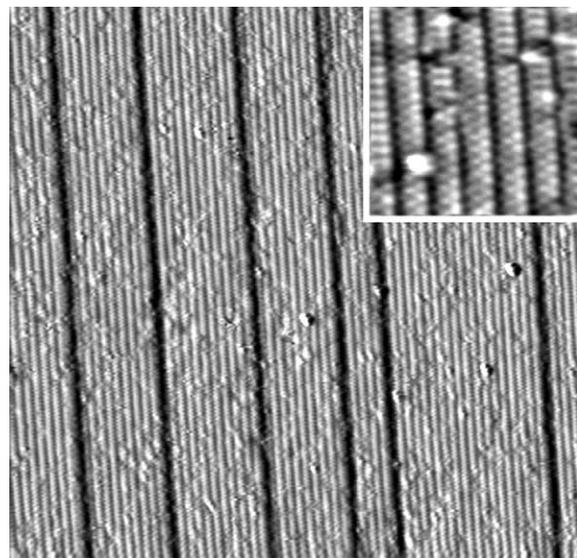
Fig. 1. One-dimensional 5×2 chain reconstruction of gadolinium on stepped Si(1 1 1), viewed by STM. The domain with the chains parallel to the step edges is singled out. The inset resolves the chains into two rows of atoms. Full panel: 100×100 nm^2 with $+1.2$ V sample bias. Inset: 11×11 nm^2 with -1.2 V sample bias.
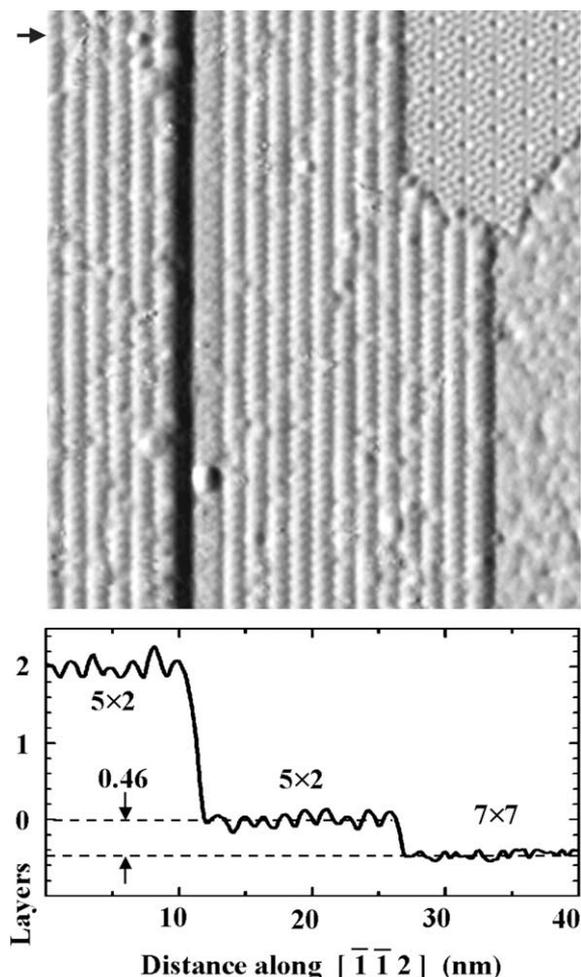
Fig. 2. Height of the Si(1 1 1)5 × 2–Gd surface relative to Si(1 1 1)7 × 7. The arrow marks the position of the line scan. (40 × 45 nm², +1.6 V sample bias. 1 layer = 0.314 nm.)

rows of atoms with a spacing of two lattice constants along the chain and across the chain. This 2 × 2 zig-zag arrangement between the two atomic rows prevails, but the c(4 × 2) ladder configuration does occur occasionally, such as in the leftmost chain. By comparison, the Si(1 1 1)5 × 2–Au surface exhibits only one row of atoms spaced by two lattice constants [3,4]. The highly stepped Si(5 5 7)–Au surface has two such rows, but with equal probabilities for the zig-zag and ladder configurations [9]. Both of the Au structures display a low density of atomic protrusions in lattice sites between the chains (0.02 monolayer for Si(1 1 1)5 ×

2–Au and 0.01 monolayer for Si(5 5 7)–Au). There is no analog of those for Si(1 1 1)5 × 2–Gd. Defects in the Gd chain structure are more random.

The height of the Si(1 1 1)5 × 2–Gd surface is determined relative to that of clean Si(1 1 1)7 × 7 in Fig. 2. The left side of Fig. 2 contains two terraces with 5 × 2-Gd chains separated by a double step, which is used as height calibration. The height scale in Fig. 2 bottom is in units of the Si(1 1 1) step height (0.314 nm). On the right is a 7 × 7 region, and on the lower right an unresolved $\sqrt{3} \times \sqrt{3}$-Gd region. Depending on sample bias, the average Si(1 1 1)5 × 2–Gd surface lies 0.2–0.6 of a step height below Si(1 1 1)7 × 7. The difference is larger at positive sample bias. For example, in Fig. 2 bottom we have the Si(1 1 1)5 × 2–Gd planes located $(1 - 0.46) = 0.54$ of a step height below the Si(1 1 1)7 × 7 planes at a bias of +1.6 V. For comparison, the Au-induced Si(1 1 1)5 × 2–Au surface lies 0.2–0.5 of a step height below Si(1 1 1)7 × 7, but the difference is largest for negative bias.

The electronic structure of Si(1 1 1)5 × 2–Gd has a very characteristic feature. When reversing the sample bias in Fig. 3 the bright ridges of the 5 × 2 structure shift by half a unit cell, thereby inverting the contrast between valleys and ridges. Nearby patches of the 7 × 7 reconstruction undergo the well-known change of contrast from filled to unfilled states (Fig. 3a, left), but do not shift laterally as observed for 5×2-Gd. Likewise, the edge of a silicide island in Fig. 3b (center) continues perfectly straight when reversing the bias. The shift of the 5 × 2–Gd chains indicates that filled states and empty states are located on alternating atomic rows. Such a lateral separation of charge reflects an ionic character. This feature distinguishes Si(1 1 1)5 × 2–Gd from the Au-induced chain structures. There are additional, finer differences between the images at opposite sample bias. A well-defined zig-zag chain of filled orbitals is seen with negative sample bias (Fig. 1 inset and Fig. 3a,b bottom). The empty orbitals observed between the zig-zag chains at positive bias are less resolved (Fig. 2 and Fig. 3a,b top).

For higher Gd coverage on Si(1 1 1) we find two further surface reconstructions. First, a $\sqrt{3} \times \sqrt{3}$ structure is formed, similar to the finding for Au on Si(1 1 1). A patch of it is seen in the lower right of Fig. 3. A further increase in coverage leads to
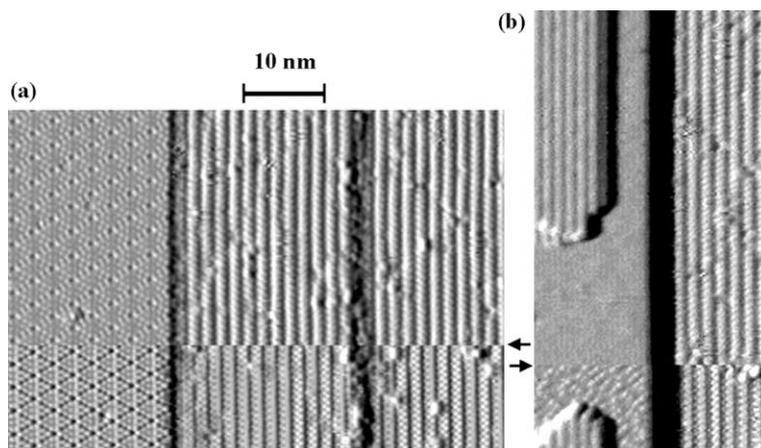
Fig. 3. Spectroscopic imaging of Si(1 1 1)5 × 2–Gd. An inversion from ridges to valleys is observed along the line where the sample bias is reversed (arrows). The bias voltage is −1.2 V below and +1.2 V above the line. The corner holes of Si(1 1 1)7 × 7 in (a) are still lined up and the edge of the GdSi$_2$ island in (b) remains straight. (a) Si(1 1 1)7 × 7 (left third), together with Si(1 1 1)5 × 2–Gd (two thirds on the right). (b) GdSi$_2$ island with 4 × 1 chains on top (left half), together with Si(1 1 1)5 × 2–Gd (right half).

the formation of a silicide, which is most likely GdSi$_{2-x}$ judging from previous work on silicide formation with rare earths [13,14]. This phase appears in Fig. 3b (left half) as a flat surface with little corrugation. On top of the silicide grows another one-dimensional structure consisting of chains with 4 × 1 periodicity. These structures will be discussed in more detail in the context of silicide nanowire formation [15].

In summary, we have found a one-dimensional chain structure of Gd on Si(1 1 1) using scanning tunneling microscopy and spectroscopy. It exhibits two special features that distinguish it from other chain structures on silicon, i.e., the large magnetic moment of the Gd 4f electrons and the pronounced ionicity of the chains, which consist of alternating rows of empty and filled orbitals.

Acknowledgements

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