Unveiling new systematics in the self-assembly of atomic chains on Si(111)

C. Battaglia, H. Cercellier, C. Monney, L. Despont, M.G. Garnier, P. Aebi
Institut de Physique, Université de Neuchâtel, 2000 Neuchâtel, Switzerland
E-mail: corsin.battaglia@unine.ch

Abstract. Self-assembled arrays of atomic chains on Si(111) represent a fascinating family of nanostructures with quasi-one-dimensional electronic properties. These surface reconstructions are stabilized by a variety of adsorbates ranging from alkali and alkaline earth metals to noble and rare earth metals. Combining the complementary strength of dynamical low-energy electron diffraction, scanning tunneling microscopy and angle-resolved photoemission spectroscopy, we recently showed that besides monovalent and divalent adsorbates, trivalent adsorbates are also able to stabilize silicon honeycomb chains. Consequently silicon honeycomb chains emerge as a most stable, universal building block shared by many atomic chain structures. We here present the systematics behind the self-assembly mechanism of these chain systems and relate the valence state of the adsorbate to the accessible symmetries of the chains.

1. Introduction
Stimulated by their great potential for next generation electronic, magnetic, optical and chemical devices, research on ordered nanostructures has attracted tremendous interest. Their fabrication remains a challenging task. Spontaneous self-assembly represents a promising bottom-up approach, which allows to fabricate nanostructures in a massively parallel fashion. Understanding the mechanisms underlying spontaneous nanostructure formation is crucial for establishing control over their dimensions, spatial distribution and uniformity. Here we address the self-assembly of macroscopic arrays of atomic chains on silicon surfaces which have been the focus of intense research because of their fascinating quasi-one-dimensional electronic properties [1–4]. A large variety of adsorbates ranging from alkali and alkaline earth metals to noble and rare earth metals is known to induce a reconstruction of the Si(111) surface into atomic chains. Most chain structures are based on a common structural backbone formed by silicon atoms. The role of the adsorbate is to stabilize these silicon chains by donating the correct number of electrons. We recently showed that besides monovalent and divalent adsorbates, trivalent adsorbates are also able to stabilize Si atomic chains [5]. In this paper we first review the structure for the monovalent and divalent adsorbates and then introduce the extension to the trivalent adsorbates. This new piece of information allows us to understand new aspects of the systematics behind the self-assembly process, from which we can draw conclusions about the accessible symmetries of the chains.
2. Monovalent adsorbates

Monovalent adsorbates such as alkali metals (Li, Na, K, Rb, Cs) together with Ag are known to induce a chain reconstruction on Si(111) exhibiting a (3×1) superstructure. The widely accepted structural model, the so-called honeycomb chain-channel (HCC) model [6–8], is shown in Fig. 1a). The (3×1) unit cell (black) and its relation to the (1×1) surface unit cell (grey) of the (111) oriented substrate is shown as well. The HCC model consists of Si honeycomb chains running along the [1\bar{1}0] direction separated by empty channels. The structure contains five threefold coordinated, thus under-coordinated, silicon atoms per (3×1) unit cell. Each of the five associated silicon dangling bonds, marked schematically by the red symbols in Fig. 1a), gives rise to a surface state. A total of five electrons, one from each dangling bond, is available to fill these states. Since each surface state is able to accommodate a maximum of exactly two electrons, we get two completely filled surface states below the Fermi energy, one half-filled metallic surface state crossing the Fermi energy and two empty states. However, in order to stabilize the HCC structure one more electron is required. This additional electron, which is provided by the adsorbate atom, allows an enormous energy gain by completely filling the metallic state, rendering it insulating by bringing it below the Fermi energy [8]. The adsorbate atoms, represented by blue disks in Fig. 2a), are occupying the sites inside the channels. Since one electron per (3×1) unit cell is required, there is one monovalent adsorbate per (3×1) unit cell and thus the adsorbate coverage is 1/3 monolayer (ML).

3. Divalent adsorbates

Silicon honeycomb chains may also be stabilized by divalent adsorbates such as the alkaline earth metals (Mg, Ca, Sr, Ba) and rare earth metals (Sm, Eu, Yb) [9]. Although these rare earth metals commonly occur in a +3 valence state, a +2 configuration is occasionally preferred as in this case. Since a divalent adsorbate provides twice as many electrons compared to a monovalent adsorbate, only 1/6 ML, i.e. half the monovalent adsorbate coverage is required [10]. Consequently only every second site in the channel is occupied leading to a doubling of the unit cell size along the chain direction (see Fig. 2b). Thus for divalent adsorbates the unit cell has a (3×2) symmetry. In LEED patterns however, instead of sharp ×2 spots, only faint half-order streaks parallel to the ×3 spots are observed. These are caused by the occurrence of two consecutive empty sites in the channel. Such a defect leads to a registry shift of the adsorbate sequence in one channel with respect to adsorbates in the adjacent channel by one period along the chain direction. Since adsorbates in adjacent channel are only very weakly coupled, the two configurations are energetically almost degenerate. The local mixing of these
Figure 2. Systematics of adsorbate induced silicon chains. Adsorbate atoms are drawn in blue. Valence of the adsorbate, symmetry of the unit cell, top and side view of the atomic structure are shown. The line labeled electron counting, shows how the final unit cell can be decomposed into the basic building blocks. The number inside each unit cell gives the number of electrons required to stabilize each building block. The last line gives the adsorbate coverage for each structure.

At intermediate coverages, divalent adsorbates stabilize chain structures with $(5\times2^\ast)$, $(7\times2^\ast)$ and even $(9\times2^\ast)$ depending on the adsorbate. These are considered to be composed of an appropriate combination of honeycomb chains and Seiwatz chains. For the $(5\times2^\ast)$ symmetry for instance shown in Fig. 2c), a honeycomb chain alternates with a Seiwatz chain. The $(5\times2^\ast)$ unit cell can be thought of as being composed of two honeycomb unit cells with $(3\times1)$ symmetry plus two Seiwatz unit cells with $(2\times1)$ symmetry as schematized in Fig. 2c). The adsorbates have to donate one electron for each of the two honeycomb units plus two electrons for each of the two Seiwatz units. Thus the adsorbates have to provide a total of six electrons per $(5\times2^\ast)$ unit cell. This condition is easily satisfied by placing three divalent adsorbates per $(5\times2^\ast)$ in between the Si chains resulting in a coverage of $3/10$ ML. For the $(7\times2^\ast)$ and the $(9\times2^\ast)$ symmetry shown in Fig. 2d) and 2e) a honeycomb chain alternates with two respectively three successive...
Seiwatz chains, requiring the adsorbates to provide 10 respectively 14 electrons, resulting in an adsorbate coverage of 5/14 respectively 7/18 ML. Note that these intermediate symmetries are not accessible to monovalent adsorbates, since it requires the stabilization of Seiwatz chains.

4. Trivalent adsorbates

For trivalent adsorbates such as Gd [14], but also Dy [15], Er [16], Ho [17] chain reconstructions with (5×"2") symmetry have been observed. To construct the (5×"2") unit cell, we combine once again a honeycomb chain with a Seiwatz chain (see Fig. 2g). The required six electrons are easily obtained by placing two trivalent adsorbates per unit cell in the channels. Note that for the divalent adsorbates, we had to take three adsorbates to satisfy the doping criterion. The resulting coverage for the trivalent adsorbates is 2/10 ML, a value which is consistent with experiment [14]. It is important to emphasize that besides the (5×"2") symmetry no other symmetry has been observed for the trivalent adsorbates. Our model gives an easy explanation: the (7×"2") and the (9×"2") symmetry require 10 respectively 14 electrons to be stabilized - a condition which can not be satisfied by a trivalent adsorbate. Thus electron counting provides an intuitive picture for the occurrence of the various allowed symmetries.

5. Conclusion

Self-assembly of atomic chains on silicon surfaces is driven by the elimination of dangling bonds. Most chain structures share a common building block formed by silicon atomic chains. The fact that only silicon atoms participate in the formation of the chains allows a variety of adsorbates to adopt these one-dimensional nanostructures. Using a simple electron counting model, we are able to relate the valence state of the adsorbate to the accessible symmetries of the chains.

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