Formation of Atom Wires on Vicinal Silicon

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The feasibility of creating atomic wires on vicinal silicon surfaces via pseudomorphic step-edge decoration has been analyzed for the case of Ga on Si(112). Scanning tunneling microscopy and density functional theory calculations indicate the formation of Ga zigzag chains intersected by quasiperiodic vacancy lines or "misfit dislocations." This structure strikes a balance between the system's drive towards chemical passivation and its need for strain relaxation in the atom chains. Spatially fluctuating disorder, intrinsic to the reconstruction, originates from the two symmetry-degenerate orientations of the zigzag chains on vicinal Si.

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Deposition of submonolayer amounts of metal atoms on vicinal silicon surfaces often results in the self-assembly of single-atom chains into "atomic wire arrays" [1]. The basic idea is that incoming atoms should preferentially adsorb at the highly reactive step edges and form parallel chains of metal atoms. The transport properties of atom chains are currently of great interest because the Fermi liquid (FL) theory is expected to break down in one dimension (1D) [2]. Photoemission from gold-induced atomic chains on Si(557) [3] and Si(553) [4] revealed dispersive metallic bands that are strongly one dimensional, and, despite the fact that clear deviations from FL theory have not yet been discerned, these systems are being vigorously pursued as their electronic properties are highly tunable and indeed very remarkable [1].

Interestingly, atomic chain structures on semiconductor surfaces always seem to exhibit some spatially fluctuating disorder. For instance, excess adatoms on Si(111)-5 × 2-Au, presumably Si, electrically dope the quasi-one-dimensional parent band structure [5]. Similar observations have been made on Au-covered high-index Si surfaces [6], and the argument has been made that their presence is electronically driven to help stabilize the chain structure. Alternatively, random registry shifts in alkaline-earth atomic chains are an example of entropy driven disorder [7]. Defects in these quasi-1D arrays mostly appear intrinsic to the surface reconstruction and often assume quasiperiodic arrangements. Their presence should strongly affect electronic transport through the atom wires. Though it remains to be seen whether self-assembly of atom wires on surfaces will ever lead to a practical device, it is becoming increasingly clear that such arrays serve as powerful model systems not only to study 1D transport and possible formation of a Luttinger liquid [2], but also to study aspects of chemical stability and the role of the ubiquitous symmetry breaking defects in the formation mechanism and electronic properties of surface nanostructures.

In this Letter, we explore atom-wire formation for the case of Ga on Si(112) [8–12]. In this surface, quasiperiodic misfit dislocations or vacancy lines (see Fig. 1), orthogonal to the atom chains, relieve compressive strain [11] and produce a quasi-6 × 1 periodicity [10]. Scanning tunneling microscopy (STM) experiments and first-principles density functional theory (DFT) calculations show that the atom chains consist of Ga zigzag chains rather than linear atom chains, a result that can be easily understood from the system's tendency to passivate all its dangling bonds. The quasiperiodicity or meandering of the vacancy lines is caused in part by thermal fluctuations around the ideal 6 × 1 superstructure [10,13]. However, "intrinsic fluctuations" exist within the ideal 6 × 1 subunits which are solely a consequence of the twofold symmetry of the vicinal template for atom-wire growth.

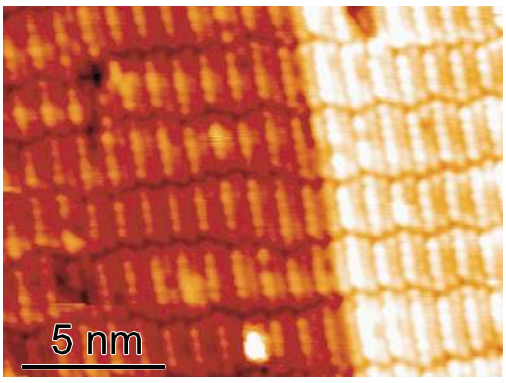

FIG. 1 (color online). Large scale empty-state STM image of the Si(112)6 × 1-Ga surface. Tunneling conditions: 2.0 V, 0.1 nA.

Thus the highly complex appearance of this 1D atom wire can be understood in great detail from the drive towards chemical passivation, formation of misfit-strain dislocations, and domain degeneracy.

Experiments were carried out in an ultrahigh vacuum system (base pressure $<5 \times 10^{-11}$ mbar) with a Ga deposition source, direct current sample heating facilities, and a variable temperature STM. The sample was flashed at 1475 K to remove the native oxide. During resistive heating, the current was directed parallel to the nanofacets of the clean (112) surface (i.e., in the $[1\bar{1}0]$ direction) in order to avoid current-induced step bunching. In the "one-step" fabrication procedure, Ga is evaporated onto Si(112) kept at a substrate temperature of $T_s = 825$ K [9]. In the "two-step" procedure, Ga is deposited onto Si(112) at room temperature. After depositing more than 1 ML, the substrate is annealed to $T_s = 825$ K to remove excess Ga and form the 6×1 structure [10]. Both procedures produced identical 6×1 low energy electron diffraction patterns and STM results. STM experiments were performed at room temperature and at ~40 K using etched tungsten tips.

Figure 1 shows a large scale empty-state STM image of the Si(112)6×1-Ga surface. Parallel atomic lines along $[1\bar{1}0]$ are intersected by dark vacancy lines. The vacancy lines are not straight; as discussed below, this is due to the coexistence of 6×1 and 5×1 units in the surface [11,13], and to the presence of *intrinsic* fluctuations in the vacancy lines. Figure 2(a) shows an atomic resolution empty-state STM image of a 6×1 Ga/Si(112) surface. The brightest atomic lines in Fig. 2(a) are the same atomic lines as imaged by Baski *et al.* [10]. But due to better STM resolution, we also observe an atomic line lying between the brighter lines (see also Fig. 1). These two parallel atomic lines appear to form a *zigzag* pattern, resulting in a *zigzag asymmetry* in the vacancy line. In the filled-state image, Fig. 2(b), a relatively bright protrusion is the dominant feature. Registry aligned dual bias images show that this bright protrusion is located in the vacancy lines. Bright protrusions in different unit cells are connected by fuzzy lines along the $[1\bar{1}0]$ direction. These STM images imply that the step-edge decorated structural model [8–12] of the Si(112)6×1-Ga surface needs to be reexamined because the vacancy lines in that model have mirror plane symmetry (i.e., mirror plane perpendicular to $[1\bar{1}0]$). We thus have to consider alternative atomic arrangements and allow for the possibility of a different Ga/Si composition ratio of the surface layer. To narrow the surface stoichiometry, we performed Rutherford backscattering spectrometry (RBS) experiments. Surprisingly, the RBS absolute coverage measurement indicated 9 ± 1 Ga atoms per 6×1 unit cell, as compared to 5 Ga atoms for the step-edge decorated model.

Extensive DFT calculations were performed in order to identify the precise atomic structure of the Ga/Si(112) surface. New candidate structural models corresponding

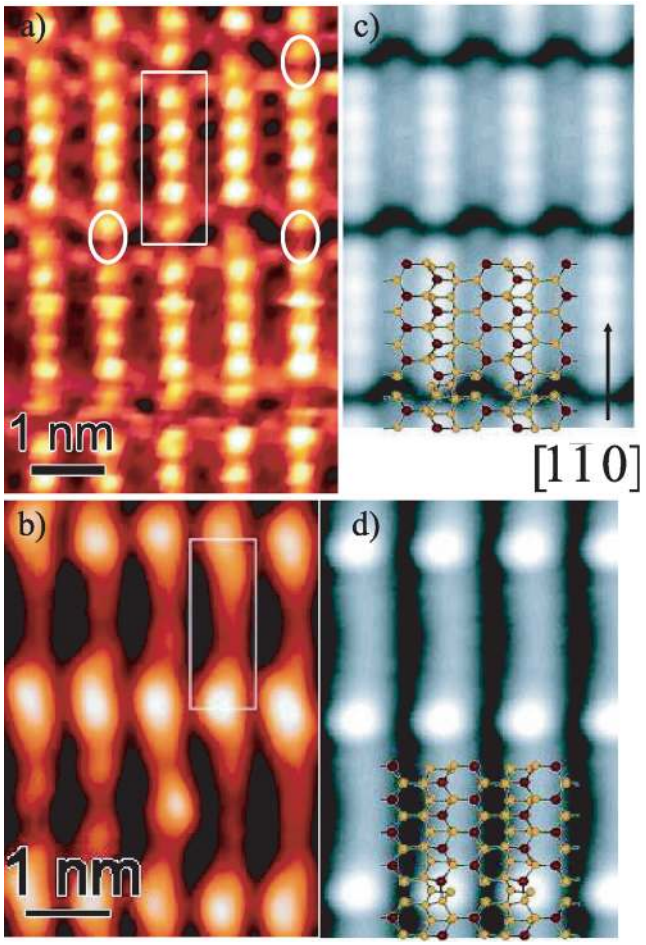

FIG. 2 (color online). (a) Empty-state STM image of the Si(112)6×1-Ga surface. Tunneling conditions: 1.5 V, 0.2 nA. The oval annotations highlight three Si-Ga dimers with one of the two possible orientations discussed in the text. The Ga atom is located in the upper half of the oval while the invisible Si atom is located in the lower half; see also Fig. 4. The 6×1 unit cell is also indicated. (b) Filled-state STM image. Tunneling conditions: -2.0 V, 0.1 nA. (c) Empty-state and (d) filled-state theoretical STM images corresponding to the surface structure of Fig. 4.

to Ga coverages ranging from 5 to 11 Ga atoms per 6×1 unit cell were explored using an efficient local-orbital DFT method [14]. In total, more than 40 new structures were fully relaxed, and their relative stability was analyzed comparing their surface energies $F = E_{\text{tot}} - \mu_{\text{Si}} N_{\text{Si}} - \mu_{\text{Ga}} N_{\text{Ga}}$: since different surface structures contain different numbers of Ga and/or Si atoms we have to consider also the Ga and Si chemical potentials μ_{Ga} and μ_{Si} (E_{tot} is the total energy per 6×1 unit cell, and N_{Si} and N_{Ga} are the number of Si and Ga atoms per 6×1 unit cell). For μ_{Si} we have used the total energy of bulk Si, and we have analyzed the stability of the different surface structures as a function of μ_{Ga}. The most promising surface structures were further refined using a plane-wave DFT code [15]. Figure 3 shows the surface energy as a function of μ_{Ga}, for the most stable surface structures

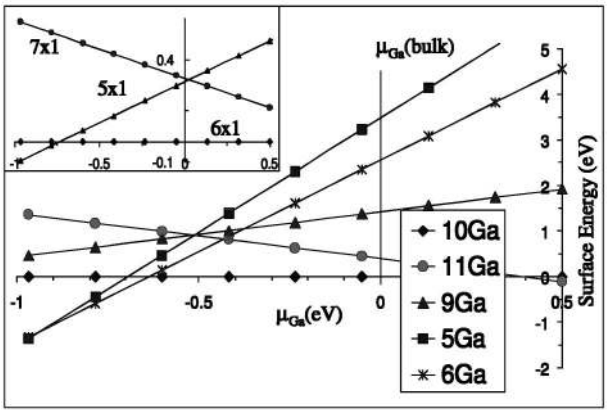

FIG. 3. Surface energy as a function of μ_{Ga} for the most promising Si(112)6 × 1-Ga candidate structures. The structure with 10 Ga atoms per 6 × 1 unit cell (see Fig. 4) is used as reference. Inset: analysis of the stability of the zigzag structure (Fig. 4) with respect to the longitudinal periodicity. Note the different vertical scale (also in eV).

containing 5, 6, 9, 10, and 11 Ga atoms [16]. The chemical potential of bulk Ga, $\mu_{\mathrm{Ga}}(\mathrm{bulk})$, can be expected to be the upper limit for μ_{Ga} [10]. A lower limit to the actual chemical potential μ_{Ga} of the overlayer can be estimated from the experimental conditions. Consider the one-step process in which the (6 × 1) phase is formed under a Ga flux at a sample temperature of $T_s = 825$ K. At this temperature the incoming flux is balanced by a flux of Ga atoms desorbing from the surface and the sample can be considered to be in thermodynamic equilibrium. Approximating the chemical potential in the effusion cell by the total energy of bulk Ga, $\mu_{\mathrm{Ga}}(\mathrm{bulk})$, the overlayer chemical potential can be estimated from

$$\mu_{\mathrm{Ga}} = \mu_{\mathrm{Ga}}(\mathrm{bulk}) - k_B T \ln\left(\frac{p_c}{p_s}\right),$$

where p_c is the Ga vapor pressure in the effusion cell and p_s the Ga vapor pressure at the sample. We obtain [17] $\mu_{\mathrm{Ga}} = \mu_{\mathrm{Ga}}(\mathrm{bulk}) - 0.32(0.48)$ eV.

In Fig. 3 we observe that the structure with 10 Ga atoms per 6 × 1 unit cell is the most stable for this range of μ_{Ga}, in good agreement with the experimental RBS value. As shown in Fig. 4 the Ga atoms in this surface form two parallel rows: a row of "step-edge"-Ga atoms adsorbed at the (111)-like step and a second row of Ga atoms adsorbed at the terraces. The two Ga rows form a zigzag pattern. Each Ga row contains 5 Ga atoms per 6 × 1 unit cell; i.e., there is a Ga vacancy in each row. Vacancies in different Ga rows line up and form vacancy lines [13]. The creation of Ga vacancies (and concomitant breaking of the Ga backbonds) is compensated by the formation of a Si-Ga dimer at the step edge and a neighboring Si-Si dimer in the terrace row; both dimer bonds are parallel to the $[1\bar{1}0]$ direction. In this zigzag structure all the partially filled Si dangling bonds are replaced by empty Ga dangling bonds, and the surface is semiconducting. Evidently, the system's

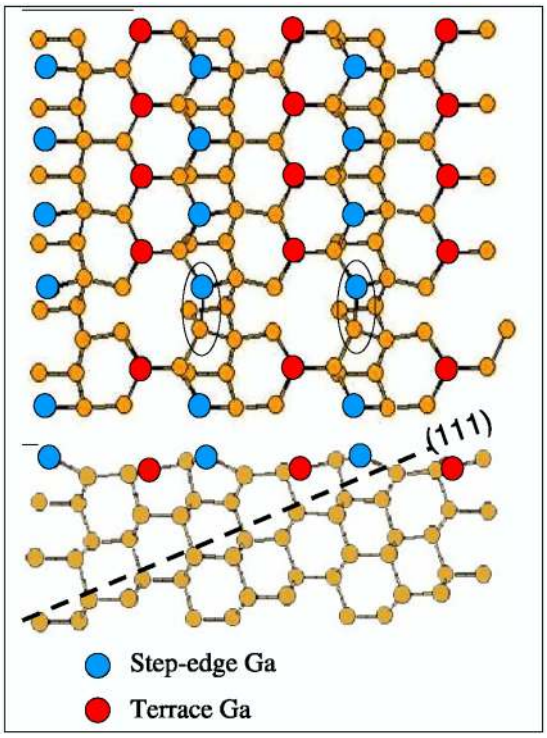

FIG. 4 (color online). Ball and stick representation of the energy minimized structure (zigzag model) for the Si(112)6 × 1-Ga surface. Top view and side view. Ovals enclose the Si-Ga dimers.

desire to passivate all dangling bonds precludes the formation of metallic single-atom wires at the step edges. Vacancy-line creation is driven by the need to relieve the compressive strain along $[1\bar{1}0]$ [11].

Figures 2(c) and 2(d) show simulated STM images [18] for the zigzag model with a top view of the structural model superimposed. The agreement between the experimental and theoretical STM images is excellent. It shows that the two atomic lines seen in the empty-state STM images are the step-edge and the terrace Ga lines; the zigzag asymmetry in the vacancy lines observed experimentally is neatly reproduced by the simulated STM images. In the filled-state image, fuzzy lines with a bright protrusion inside the vacancy line are observed, also in agreement with the experimental images. The bright protrusion originates from the Si-Ga dimer in the vacancy lines, while the fuzzy lines are due to Si-Ga bonds on the (111)-like terrace, close to the step edge.

The spacing between the vacancy lines often deviates from the perfect 6 × 1 periodicity. An explanation in terms of competing longitudinal periodicities was considered by Erwin *et al.* for the step-edge decorated model [11]. It was found that the 6 × 1 structure competes with 5 × 1 and 7 × 1 periodicities. We repeated this analysis for the new zigzag model (Fig. 4): the result is shown in the inset of Fig. 3. For the relevant range of μ_{Ga} the 6 × 1 periodicity is the most stable, while the 5 × 1 periodicity is only 0.1–0.2 eV/(6 × 1 unit cell) higher. This explains

the presence of local 5×1 units in the STM images [10,12] that causes the meandering of the vacancy lines, similar to the well-known meandering of dimer-vacancy lines in Ge/Si(100) heteroepitaxy [13]. However, the current structural model of Ga/Si(112) also implies the possibility of intrinsic fluctuations, i.e., fluctuations within each 6×1 or 5×1 domain. For example, a closer scrutiny of the empty-state STM image of Fig. 2(a) reveals that in this pure 6×1 region the number of *step-edge Ga atoms* between the vacancy lines fluctuates between four and six while the number of *terrace Ga atoms* is always five. The fluctuations associated with the step-edge atoms are related to the two possible orientations of the Si-Ga dimers [in Fig. 2(a) there are a total of nine Si-Ga dimers with the orientation shown in Fig. 4, and six Si-Ga dimers with the opposite orientation]. This twofold degeneracy is a direct consequence of the $[1\bar{1}0]$ mirror plane symmetry of the vicinal substrate, broken by the Si-Ga dimers. No such fluctuations can be discerned from the filled-state images since the observed bright protrusions appear in the middle of the Si-Ga dimer [see Fig. 2(d)].

We have estimated the energy associated with interchanging the atoms of the Si-Ga dimer in an ideal 6×1 reconstruction by analyzing a 12×1 unit cell with either two times 5 Ga atoms in the step-edge row between vacancy lines, or 6 and 4: our calculations show that this energy is less than $\sim$0.01 eV (per 12×1 unit cell). This small energy explains the high number of intrinsic fluctuations in the step-edge rows as observed in the empty states images.

Because nanostructures generally are nonequilibrium structures, we also investigated the possibility that the metastable step-edge decorated structure is stabilized *kinetically* through selective desorption of the Ga terrace atoms during the annealing step of the two-step process [$\mu_{\mathrm{Ga}} \ll \mu_{\mathrm{Ga}}(\mathrm{bulk})$]. Total energy calculations, however, show that the desorption energies for the Ga atoms of Fig. 4 are lower for step-edge atoms than for terrace atoms by $\sim$0.7 eV/atom. Hence, there seems to be no kinetic pathway to achieve the step-edge decorated structure via thermal processing.

In conclusion, the structure, stability, and fluctuating disorder of quasi-1D atom-wire arrays have been studied for the case of Ga on Si(112). The experimental conditions were explicitly taken into consideration through a detailed chemical potential analysis. Step-edge decoration does not appear to be a viable fabrication method for metallic atom wires, at least not for Ga on Si(112), and it is doubtful that it would work for other high-index silicon surfaces [1]. The thermodynamically stable structure instead consists of a 6×1 zigzag arrangement that passivates all dangling bonds. In addition to thermal meandering of the vacancy line giving rise to the quasi-periodic 6×1 structure, we also observe intrinsic fluctuations that can be understood on symmetry grounds. Thus, the highly complex appearance of the Ga/Si(112) 1D atom-wire array can be understood in surprising detail from the general principles of chemical passivation, strain relaxation, and domain degeneracy. By combining STM methods with state-of-the-art DFT codes and powerful computing resources, similar analysis should be within reach to explore structure, composition, and fluctuations, all in the context of the relevant experimental fabrication parameters, for a wide variety of surface nanostructures.

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[16] The 5 Ga case corresponds to the step-edge decorated linear chain of Ga atoms; the other cases are zigzaglike structures. Details of these and other structures will be presented in a forthcoming paper.
[17] Since the effusion cell flux is proportional to its vapor pressure, p_c, times the cell aperture area, and the sample flux is also proportional to its corresponding vapor pressure, p_s, times the sample area, we conclude that $(p_c/p_s) \sim 10^2(10^3)$.
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