# Hexagon versus Trimer Formation in In Nanowires on Si(111): Energetics and Quantum Conductance

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The structural and electronic properties of the quasi-one-dimensional In/Si(111) surface system are calculated from *first principles*. It is found that the symmetry lowering of the In chains is energetically favorable, provided neighboring nanowires are correlated, giving rise to a doubling of the surface unit cell both along and perpendicular to the chain direction. The recently suggested formation of hexagons within the In nanowires [C. González, F. Flores, and J. Ortega, Phys. Rev. Lett. **96**, 136101 (2006)]—in clear contrast to the trimer formation proposed earlier—drastically modifies the electron transport along the In chains, in agreement with experiment.

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One-dimensional (1D) electronic systems are currently intensively investigated for fundamental interest—their physics is rather different from the two- or three-dimensional cases—as well as for technological reasons: Because of the rapid miniaturization of electronic devices, (quasi)-1D structures may soon be utilized as atomic-scale interconnects. Therefore, there is presently an intense search for real quasi-1D systems with internal atomic structures that allow for studying the properties of such devices in detail.

In this context, the adsorption of indium on Si(111) is a popular model system. The room temperature (RT) monolayer adsorption leads to self-assembled In ''nanowires'' along the $[\bar{1}10]$ direction separated by about 3.8 Å. The adsystem has a $4 \times 1$ translational symmetry. Based on x-ray diffraction data [1] and total-energy calculations [2], a structural model was developed that largely explains the observed electronic properties, optical response, and scanning tunneling microscopy (STM) images [3–10]: Each nanowire consists of two zigzag chains of In atoms, with the edge In atoms adsorbed in $H_3$ and $T_4$ sites (at an ''up'' position) and the inner In atoms at bridge sites (at a ''down'' position). The nanowires are separated by zigzag Si chains resembling the $\pi$-bonded chains of the clean Si(111)-$(2 \times 1)$ surface; see Fig. 1.

The low-temperature (LT) structure of this system and its properties are controversial: Below about 125 K, a reversible temperature-induced phase transition leads to a $8 \times 2$ surface periodicity clearly seen in STM [11–16]. The precise nature of the phase transition and its driving forces, however, is unclear. It has been suggested that the transition is driven by a single-band [11] or triple-band [13] Peierls instability or by a simple energy lowering due to a periodic lattice distortion [2,6–8,17]. While the RT $4 \times 1$ phase is a quasi-1D metal [18] that gives rise to electron transport attributed to In-related surface states [12,18,19], many experimental studies conclude that the phase transition leads to a fundamental energy gap of 0.1–0.3 eV [11–14]. Others state only a reduced density of states at the Fermi energy ($E_F$) [15,17,20] or remain inconclusive [21]. In any event, the electron conduction through the nanowires ceases for the LT phase [12,19], and the Drude tail in high-resolution electron-energy loss spectra is drastically reduced [22].

Most *ab initio* calculations [2,5–9], however, find no gap opening upon phase transition. They predict the pairing of the outermost atoms in the zigzag subchains and the formation of trimers. These structural changes open pseudogaps in the triple-band structure, but one surface band still crosses the Fermi level. In contrast to that, recent calculations by the Flores group [23] obtained a different surface ground state: Shear distortions in neighboring In chains—indicated in Fig. 1—allow for the formation of In hexagons in a $4 \times 2$ surface periodicity. This structure was found to be insulating. The metallic $4 \times 1$ surface observed at RT was explained by dynamic fluctuations between degenerate ground states [24].

Here we compare the energetics and quantum conductance of the newly proposed hexagon model with the trimer formation on the basis of *first-principles* calculations. We

 

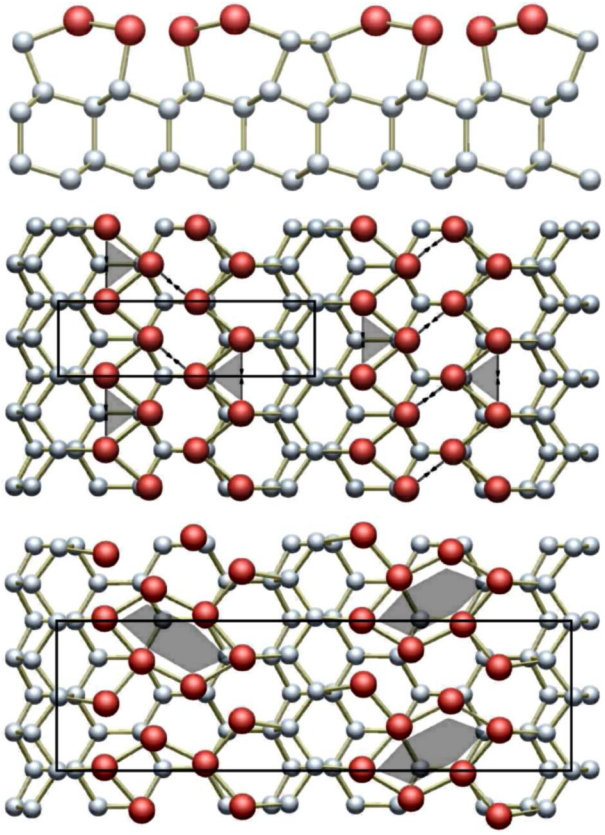

FIG. 1 (color online). Side and top views of the ideal, unreconstructed In/Si(111)-(4 × 1) surface (upper two panels) and the hexagon formation within 8 × 2 translational symmetry (lower panel). The dimerization and shear movements as well as trimer and hexagon orientation are indicated by arrows and shaded polygons, respectively.

find the potential energy surface (PES) to be very flat and extremely sensitive with respect to the details of the calculation. In contrast to Refs. [23,24], the correlation between neighboring In chains is found to be necessary to stabilize the In hexagons. The electron transport through the In nanowires depends strongly on the structural details of the chains. The transmission of the hexagon model vanishes for a small energy window at $E_F$.

Our results are obtained using density functional theory (DFT) within the local density as well as generalized gradient approximation (LDA/GGA) [25,26] for exchange and correlation (XC) as implemented in the Vienna Ab-initio Simulation Package (VASP) [27]. The electron-ion interaction is described by ultrasoft non-normconserving pseudopotentials. We also tested projector-augmented wave potentials, but no significant changes were noted. There is, however, an influence of the In 4*d* electrons on the surface energetics. It is studied by either treating them as valence states or freezing them into the core. The In/Si(111)-(4 × 1), (4 × 2), and (8 × 2) surfaces are simulated by repeated asymmetric slabs with six Si bilayers and a vacuum region equivalent in length. Hydrogen is used to saturate the bottom sides of the slabs. The **k**-space integrations are performed using uniform meshes equivalent to 32 points in the Brillouin zone of the 4 × 1 surface. The coherent electron transmittance along the In wires has been computed using the WanT approach [28], i.e., a Green function formalism based on "maximally localized Wannier functions" [29] as a minimal basis set. Thereby, we exploit the fact that the In-related surface states close to $E_F$ depend very little on the substrate [30]. Test calculations where the Si substrate was modeled by one and two Si bilayers show that the electron transport is indeed well described by model structures that contain only the In and nearest neighbor Si atoms with the remaining Si dangling bonds terminated with hydrogen.

The structure with two ideal zigzag chains belonging to one In nanowire parallel to the $[1\bar{1}0]$ direction (upper two panels in Fig. 1) is a local minimum of the surface energy. The displacement of the outer In atoms by about 0.2 Å towards each other—as indicated by vertical arrows in Fig. 1—to form pairs and finally trimers with one of the inner atoms gives rise to another, nearly degenerate local minimum on the PES. The shear movement of the inner In atoms required to form hexagons is hindered by an energy barrier. After enforcing this displacement, a new energy minimum is reached, where the distance of two inner In atoms is reduced from 3.12 to 2.96 Å [31]. The antiphase arrangement of hexagons or trimers in neighboring wires leads to the doubling of the unit cell perpendicular to the wires.

Figure 2 shows the change of the surface energy relative to the 4 × 1 geometry upon hexagon formation [32]. The calculations were performed within the LDA and keeping the In 4*d* electrons frozen. It is clear from the figure that the formation of hexagons in phase, i.e., in the 4 × 2 translational geometry, is energetically unfavorable. This finding supports earlier theoretical work that failed to yield energy minima apart from dimerized or trimerized In chain atoms [2,3,5–9] but is in contrast to the recent findings reported in Refs. [23,24]. We do find an energetic preference of the hexagon formation, however, provided the hexagons are arranged in an 8 × 2 geometry. Furthermore, the energy

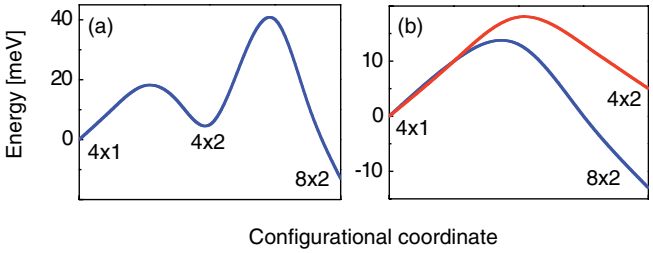


FIG. 2 (color online). Calculated (see text) energy change, for formation of hexagons, per 4 × 1 unit cell vs configurational coordinate involving (a) the "double" phase transitions 4 × 1 → 4 × 2 → 8 × 2 and (b) two "single" 4 × 1 → 8 × 2 or 4 × 1 → 4 × 2 transitions. A linear scaling between initial and final coordinates has been used to generate the intermediate geometries.

barrier for the direct transition $4 \times 1 \rightarrow 8 \times 2$ is significantly (by more than a factor of 2) lower than that via an intermediate $4 \times 2$ structure (see Fig. 2). The difference is of the order of the thermal energy at the transition temperature. Assuming conditions near equilibrium, our results indicate that the direct formation of the $8 \times 2$ phase is more likely than the appearance of an intermediate $4 \times 2$ phase. This agrees with a recent STM study that shows $4 \times 1$ and $8 \times 2$ phases coexisting [16].

When discussing the calculated energies, a word of caution is appropriate. The peculiar low-symmetry ground state of bulk In is related to subtle electronic effects and—due to its low stabilization energy of only 2 meV per atom—is easily distorted [33]. The correct simulation of the pressure-induced phase transition of bulk In requires the inclusion of the relativistic mass velocity and Darwin terms as well as the treatment of the In $4d$ states as valence electrons [34]. While the inclusion of relativistic effects is out of reach for these large surface structures, we did probe the influence of the $d$-electron treatment (core or valence) and the XC approximation (LDA or GGA). Similar to bulk In, the outcome of the calculation for substrate-supported In nanowires depends sensitively on the methodology used to describe the electron-electron interactions; see Table I. Within the GGA, the formation of trimers rather than hexagons in $8 \times 2$ symmetry is the most favored structure. This holds also in LDA, provided the In $4d$ electrons are explicitly included. Irrespective of the computational details, the antiphase arrangement of trimers or hexagons in $8 \times 2$ unit cells is favored over the corresponding arrangement in $4 \times 2$ symmetry. The formation of trimers or hexagons leads to local electron accumulation and loss. The alternating arrangement of these charge oscillations in neighboring chains lowers the surface Madelung energy. Still, the overall energy gain is very small, at most 12 meV per $4 \times 1$ unit cell according to the calculations. This explains the sensitivity of the $4 \times 1 \rightarrow 8 \times 2$ phase transition with respect to external perturbations found experimentally. Tiny amounts of impurity atoms, for example, may prevent the phase transition or even revert the LT $8 \times 2$ phase to the $4 \times 1$ surface [10,12,35]. Such a behavior seems hard to explain assuming the $4 \times 1$ structure to be a dynamic fluctuation between degenerate ground states with lower symmetry, as suggested in Ref. [24].

TABLE I. Formation energies (in meV, per $4 \times 1$ unit cell) of In/Si(111) surface reconstructions relative to the ideal $4 \times 1$ chain in dependence on the treatment of the electron XC and the explicit inclusion of the In $4d$ states.

| | GGA | | LDA | |
|---|---|---|---|---|
| Reconstruction | Core $d$ | Valence $d$ | Core $d$ | Valence $d$ |
| $4 \times 2$ hexagon | 36 | 48 | 5 | 15 |
| $8 \times 2$ hexagon | 25 | 27 | −12 | 2 |
| $4 \times 2$ trimer | 0 | 5 | 1 | 2 |
| $8 \times 2$ trimer | −0.4 | −5 | −0.5 | −0.6 |

Our findings concerning the surface energy are obviously less conclusive than the ones presented by González *et al.* [23,24]. For this reason, we now turn to a discussion of the electronic and transport properties. They are rather insensitive with respect to computational details but depend strongly on the geometry and may thus be used to identify the surface geometry. The band structures (not shown here) we obtain for the ideal $4 \times 1$ and trimer models resemble earlier work [6,8] and do not show a fundamental energy gap. The band structure calculated for the hexagon model in $4 \times 2$ symmetry reproduces largely the results by González and co-workers [24]. Remarkably, the small changes of the chain geometry and the interwire interaction upon arranging the hexagons antiphase in $8 \times 2$ symmetry lead to rather distinct changes of the band structure, in addition to the band folding. The gap between occupied and unoccupied surface states near $\Gamma$ is widened, and the fundamental gap near $X'$ shrinks and becomes more direct. Given the underestimation of the band gap within DFT [36], the calculated band gap of 0.05 eV (GGA, $4d$ in valence) is consistent with the experimental findings of 0.16 eV from STM [14] and 0.3 eV from surface conductivity measurements [12]. The position of the calculated maximum of occupied bands near $X'$ is confirmed by photoelectron spectroscopy [11,13].

In Fig. 3, we show the calculated quantum conductance of five infinite nanowires that model the In/Si(111) systems discussed above; i.e., the atomic coordinates of the In and neighboring Si atoms were taken from the relaxed surface structures (GGA, $4d$ in valence). Irrespective of the actual translational symmetry, we performed all calculations using $8 \times 2$ unit cells. Obviously, the energy-dependent transmittance is very sensitive with respect to the wire geometry, as expected from the band structures discussed above. Because of the free electrons in the metallic In wires of the In/Si(111)-$(4 \times 1)$ surface, its transmittance is nearly constant over the energy range of the Si band gap. The value obtained in our calculation somewhat overestimates—by roughly a factor of 2—the experimentally determined surface-state conductance in the RT regime [12,18,19]. This is partially an effect of the metallic contacts and their scattering [37] as well as

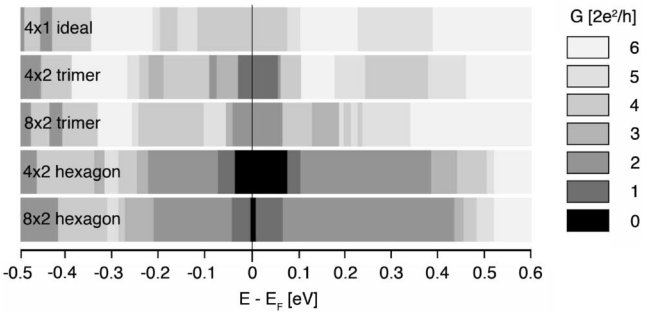


FIG. 3. Quantum conductance spectrum for electron transport along the chain direction calculated for In/Si(111) model structures; see text.

related to the thermal dissipative scattering due to phonons at finite temperature. The formation of In trimers with $4 \times 2$ or $8 \times 2$ symmetry does not quench the conductance but leads to a reduction for energies very close to $E_F$, i.e., within about $10^{-1}$ eV. For energies farther below or above $E_F$, the transmittance resembles those of the ideal chains. Only some conduction channels slightly shift in energy or are somewhat reduced in magnitude. The conductance changes upon hexagon formation are significantly more pronounced. In both the $4 \times 2$ and the $8 \times 2$ symmetry, it strongly reduces the transmittance through surface states over an energy range of nearly 1 eV. For energies of $10^{-2}$ and $10^{-1}$ eV around $E_F$—the size of these energy intervals is underestimated, see Ref. [36]—there is zero conductance for hexagons arranged in $8 \times 2$ and $4 \times 2$ symmetry, respectively. These findings may well account for the vanishing surface-state conductance measured for the LT phase [12,19] of the In nanowires.

In conclusion, our results show that the phase transition of the quasi-1D In/Si(111) system upon cooling is a complex process with a subtle energy balance that is easily perturbed. The $4 \times 2$ translational symmetry is insufficient to describe the structural and electronic changes that result from the phase transition. It is energetically not favored. Rather, a direct $4 \times 1 \rightarrow 8 \times 2$ transition occurs. Based solely on the surface energies, an unambiguous identification of the internal structure of the LT phase seems presently impossible. The calculated electronic structure and transport properties, however, give strong evidence for hexagon formation. In contrast to In atom pairing and trimerization, it opens a fundamental energy gap. The quantum conductance of infinite In nanowires that model the surface chain structures explains the change of the measured wire resistance for variations between the RT and LT phases of the In/Si(111) system, provided hexagons form. Our results demonstrate the distinct influence of small changes of the nanowire geometry on its conductance. Given the extremely flat potential energy surface, it is not difficult to envisage "1D devices" where the electron transport can be tuned at will.

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