Metal–insulator transition in one-dimensional In-chains on Si(111): combination of a soft shear distortion and a double-band Peierls instability

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Abstract. The most stable geometries for the (4 × 1) and (4 × 2) phases of the In/Si(111) surface have been reanalysed using DFT-annealing. A very efficient local orbital method (Fireball) has allowed us to explore the geometrical phase space and look for new absolute minima. The most stable theoretical structure is a new In/Si(111)-(4 × 2) geometry that presents a semiconducting band structure. This (4 × 2) surface, qualitatively very similar to the structural model proposed by Kumpf et al (2000 Phys. Rev. Lett. 85 4916), is found to be the result of the combination of a soft shear distortion, whereby the two zigzag In-rows are displaced in opposite directions along the In-chains, and a pairing of the outer In atoms associated with a double-band Peierls distortion.

The transport properties of atomic wires are currently of great interest because of their expected one-dimensional (1D) Luttinger liquid behaviour in their metallic phase. As deposition of In-atoms on Si(111) is known to form 1D chains along the (110)-direction [1], many different groups have studied this system to understand its basic geometrical structure and its transport properties. The basic information gathered about this In/Si(111) surface is the following:

(i) the system presents a reversible temperature-induced phase transition, with a (4 × 1)-structure at high temperature and a (4 × 2)-geometry (or 8 × 2) below 100–130 K [2].
(ii) This phase transition is a metal–insulator one, as the (4 × 1)-phase has been shown to be metallic and the (4 × 2) insulating, although the energy gap appearing in this case is rather small, ∼0.16–0.30 eV.

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The accepted model for the In/Si(111)-(4 × 1) atomic geometry was proposed by Bunk et al [3] on the basis of surface x-ray diffraction (SXRD) experiments. In this reconstruction, two zigzag rows of In atoms, that alternate with zigzag rows of Si atoms, form quasi-1D In-chains (see figure 1(a)). Angle-resolved photoelectron spectroscopy (ARPES) [1, 2, 4, 5] and inverse photoemission [6, 7] have revealed that the In/Si(111)-(4×1) surface is metallic, with three almost 1D metallic bands. Density functional theory (DFT) calculations [8]–[12] for the structure proposed by Bunk et al show optimized atomic coordinates that are in good agreement with the SXRD experiment [3]. In these calculations, the electronic structure presents three surface bands that cross the Fermi energy (see figure 1(b), states S1, S2 and S3), also in agreement with the photoemission [13] experimental evidence [1, 2, 4, 5].

This surface undergoes a temperature-induced reversible phase transition to a (8 × 2) structure at about 100–130 K as shown by electron diffraction experiments [2, 14] and scanning tunnelling microscopy (STM) [2, 15, 16] studies. The low-temperature (LT) phase is semiconducting, as revealed by ARPES [2, 4, 5], surface conductivity measurements [18, 19] and LT scanning tunnelling spectroscopy (STS) [16]. The atomic structure of the LT phase has been experimentally analysed: SXRD experiments [20], that indicate that the main structural change associated with the phase transition is a dimerization of the outer atoms in the In-chains (and thus the formation of In-trimers), and LEED experiments [14], that suggest that the phase transition is only accompanied by slight atomic displacements.
Different models have been proposed for explaining this metal–insulator transition. In the work of Yeom et al [2, 4], it was proposed that the LT phase is a 1D charge density wave (CDW) driven by a Peierls instability. This interpretation was questioned by Kumpf et al [20] based on their SXRD results. Cho et al [8] performed a DFT analysis of the atomic structure of the LT phase; in these calculations a structural optimization was performed, using the SXRD-trimer structure [20] as the initial geometry. Optimized (4 × 2) or (8 × 2) were found to be only \( \sim 8 \text{ meV}/(4 \times 1\text{-unit cell}) \) more stable than the (4 × 1) structure. Interestingly, although the results for the (4 × 1) surface showed good agreement with ARPES experiments [1], the (4 × 2) surface was found to be metallic. This is a very striking result suggesting that something not included in the DFT calculations is inducing the (4 × 1) \( \rightarrow \) (4 × 2) phase transition. Based on this argument, Ahn et al [5] have suggested with new experiments that a triple-band Peierls instability is the mechanism explaining the phase transition. The influence of defects on the LT structure has also been analysed. The charge ordering observed by STM around defects was presented by Park et al [16] as strong evidence of the CDW nature of the ground state, while Lee et al [17] based on their STM and DFT results, suggested that the LT (4 × 2) phase is not a band insulator, but is stabilized by many-body interactions.

In order to understand the nature of the LT broken-symmetry state, it is important first to investigate the atomic geometry of the LT phase. In this work, we have reanalysed the most stable (4 × 1) and (4 × 2) structures and have looked for new absolute minima that could have not been found previously. The atomic structure of the LT phase was investigated using a (4 × 2) unit-cell since previous studies have found that, basically, the only difference between the (8 × 2) and (4 × 2) structures is a relative parallel displacement of adjacent (4 × 2)-In chains (giving rise to the 8 × periodicity) [8, 20]. In this new analysis, we have used a very efficient DFT code (Fireball [21, 22]) that has allowed us to explore a more complete phase space. This technique has proven very successful in similar problems, such as the determination of the LT atomic structure for the Sn/Ge(111) \((\sqrt{3} \times \sqrt{3}) \leftrightarrow (3 \times 3)\) phase transition [23], or the atomic structure of complex 1D atomic wires for the case of Ga on Si(112) [24]. As our results will show, we have found a new In/Si(111)-(4 × 2) structure that is insulating and which has an absolute minimum energy, lower than the one given in [8]. We conclude that, contrary to previous suggestions, DFT calculations seem to yield both the (4 × 1) and (4 × 2) structures that explain the basic experimental evidence.

In our calculations, the Si crystal is simulated by a slab of 10 Si layers, with the In-atoms on top and H-atoms saturating the dangling-bonds of the last Si crystal layer. An \( \text{sp}^3\)-basis set of fireball orbitals [22] was used, with the following cutoff radii \( R_c \): 4.8 and 5.4 au for Si s and p orbitals, and 5.1, 5.7 au for In s and p orbitals. In the 4 × 2 calculations, we have used 32 special \( k \)-points in the (4 × 2)-Brillouin zone (BZ) (64 for the 4 × 1). In a first step we have calculated the 4 × 1-structure and checked that its geometry and energy bandstructure are in good agreement with previous DFT calculations. Figure 1(a) shows a top view of the 4 × 1-structure and figure 1(b) the band structure around the Fermi energy. The 4 × 1 band structure reproduces all the well-known results for this phase: in particular, we find three surface bands \((S_1, S_2 \text{ and } S_3)\) crossing the Fermi level. These bands are in good agreement with photoemission experiments and confirm the metallic character of this surface.

Cho et al [8] found, in their DFT calculations, a 4 × 2-reconstruction formed by the pairing of the outer atoms in the In chains, as suggested by SXRD [20]. This geometry does yield, however, a metallic band structure which resembles quite closely the (4 × 1)-electron bands mapped onto the (4 × 2) BZ. Regarding the electronic structure around the Fermi energy, the main effect of the (4 × 2) reconstruction found by Cho et al is to open an energy gap along
Figure 2. (a) Top view of the $4 \times 2$ structure. In–In bonds are drawn for distances less than 3 Å; In–In distances $d$ (in Å) are given in the column on the right. (b) The band structure presents an insulating character, with an energy gap of $\sim 0.3$ eV.

the $X$–$K$ direction just above the Fermi level; otherwise, this ($4 \times 2$)-reconstruction does not alter the metallic character of the $4 \times 1$-structure.

We have looked for other ($4 \times 2$)-reconstructions introducing a theoretical annealing in the system: first, we ‘heat’ the surface to $\sim 500$–$1000$ K introducing random initial velocities for the atoms according to a Maxwell–Boltzmann distribution; then, we allow the atoms to move for several hundreds time steps, and finally we anneal the system by removing kinetic energy at certain time steps until the system finds a local minimum [23]. Figure 2(a) shows the geometry we have found in this way as the most favourable for the ($4 \times 2$)-periodicity. The In atoms form distorted hexagons, with In–In bond lengths within the range 2.88–2.97 Å. The outer In atoms are dimerized in the direction along the chain, with a short (long) In–In distance of 3.04 (4.69) Å. This ($4 \times 2$)-structure is qualitatively very similar to the structural model proposed by Kumpf et al [20] on the basis of SXRD experiments, whose main characteristic is the formation, in the LT structure, of In trimers made up of two outer and one inner In atoms (In–In distances between 2.8 and 3.1 Å). These trimers correspond to atoms (1,2,7) and (4,5,3') in our structure shown in figure 2(a).

Figure 2(b) shows the band-structure around the Fermi energy for this ($4 \times 2$)-reconstruction, which now presents an insulating character. We obtain an energy gap of $\sim 0.3$ eV, in good agreement with the experimental energy gap (0.16 eV in STS [16], and 0.3 eV in surface conductivity measurements [18]). We have also calculated the total energy for this new ($4 \times 2$)-reconstruction and have found that it is more favourable than the ($4 \times 1$)-phase by 80 meV/(4 × 1 unit-cell) (or 10 meV/In atom); compared with the Cho et al [8] ($4 \times 2$)-reconstruction, that was
found more stable than the (4 × 1) by 8 meV/(4 × 1)-unit cell, the new structure is found to be more stable by 72 meV/(4 × 1)-unit cell.

A way of understanding this LT (4 × 2) structure is to discuss the (4 × 1)-geometry shown in figure 3(a). In this structure the two zigzag rows forming the In chains present opposite displacements of ±0.35 Å along the direction of the In-chains; due to these displacements, the inner In atoms form new bonds, resulting in the hexagons drawn in figure 3(a). In our calculations, this (4 × 1)-surface is only 8 meV/(4 × 1 unit-cell) higher in energy than the structure depicted in figure 1(a). Figure 3(b) shows the electronic band-structure for this surface. Comparing with figure 1(b), two things are worth commenting on: (a) the band S1 has been shifted upwards in energy, in such a way that it does not cross the Fermi level; (b) bands S2 and S3 now cross the Fermi level at almost the same wavevector, very close to the middle of the Γ − X′ direction (the X′ point). This (4 × 1)-structure appears to be created by a soft shear motion of the two In zigzag rows; moreover, this deformation creates a band-structure that favours a double-band Peierls distortion.

In figure 4 we present a comparison of the band structures along the Γ − X′ direction for the three In/Si(111) structures discussed in this paper, showing how the different atomic distortions yield an insulating band structure. In the case of the two (4 × 1)-structures, we have mapped the S1, S2 and S3 bands into the (4 × 2)-BZ. The soft shear distortion of figure 3(a) shifts the band S1 upwards, creating a gap at the Γ (or X) point, and changes bands S2 and S3 in such a way that now
they cross the Fermi energy very close to the X’ point (see figures 4(a) and (b)). This prompts a two-band Peierls distortion that takes the (4 × 1) structure of figure 3(a) to the insulating (4 × 2) structure shown in figure 2(a), opening gaps at the X’-point for bands S2 and S3 (figure 4(c)). In this Peierls distortion, the outer In atoms dimerize, similar to the atomic displacements found by Kumpf et al [20].

In conclusion, we have shown using a theoretical annealing based on an efficient local orbital DFT approach that the minimum energy In/Si(111)-(4 × 2) reconstruction appears as a result of two displacements: a soft shear motion of the two In zigzag rows, and a double-band Peierls distortion. The main electronic effect of the shear distortion is to locate the band S1 above the Fermi level; the effect of the Peierls distortion is to open a gap at the X’-point for bands S2 and S3. The result of both distortions is the formation of a stable insulating structure.

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References

[1] Abukawa T et al 1995 Surf. Sci. 325 33
[2] Yeom H W et al 1999 Phys. Rev. Lett. 82 4898
[3] Bunk O et al 1999 Phys. Rev. B 59 12228
[4] Yeom H W et al 2002 Phys. Rev. B 65 241307
[5] Ahn J R et al 2004 Phys. Rev. Lett. 93 106401
[6] Hill I G and McLean A B 1997 Phys. Rev. B 56 15725
[7] Hill I G and McLean A B 1999 Phys. Rev. B 59 9791
[8] Cho J-H, Oh D-H, Kim K S and Kleinman L 2001 Phys. Rev. B 64 235302
[9] Miwa R H and Srivastava G P 2001 Surf. Sci. 473 123
[10] Nakamura J, Watanabe S and Aono M 2001 Phys. Rev. B 63 193307
[11] Bechstedt F, Krivosheeva A, Furthmüller J and Stekolnikov A A 2003 Phys. Rev. B 68 193406
[12] Wang S, Lu W, Schmidt W G and Bernholc J 2003 Phys. Rev. B 68 035329
[13] Einstein A 1905 Ann. Phys., Lpz. 17 132
[14] Mizuno S, Mizuno Y O and Tochihara H 2003 Phys. Rev. B 67 195410
[15] Morikawa H, Matsuda I and Hasegawa S 2004 Phys. Rev. B 70 085412
[16] Park S J, Yeom H W, Min S H, Park D H and Lyo I-W 2004 Phys. Rev. Lett. 93 106402
[17] Lee G, Yu S-Y, Kim H and Koo J-Y 2004 Phys. Rev. B 70 121304 (R)
[18] Tanikawa T, Matsuda I, Kanagawa T and Hasegawa S 2004 Phys. Rev. Lett. 93 016801
[19] Uchihashi T and Ramsperger U 2003 Surf. Sci. 532–535 685
[20] Kumpf C et al 2000 Phys. Rev. Lett. 85 4916
[21] Jelinek P et al 2005 at press
   Lewis J P et al 2001 Phys. Rev. B 64 195103
   Demkov et al 1995 Phys. Rev. B 52 1618
[22] Sankey O F and Niklewski D J 1989 Phys. Rev. B 40 3979
[23] Ortega J, Pérez R and Flores F 2000 J. Phys.: Condens. Matter 12 L21
[24] Gonzalez C et al 2004 Phys. Rev. Lett. 93 126106