

Adsorption-enhanced reactivity of the In/Si(001) systemM. W. Radny,¹ P. V. Smith,¹ and L. Jurczykyszyn²¹*School of Mathematical and Physical Sciences, The University of Newcastle, Callaghan 2308, Australia*²*Institute of Experimental Physics, University of Wrocław, pl. Maxa Borna 9, Wrocław, Poland*

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The adsorption of In atoms on the clean Si(001) surface as a function of In coverage is studied using density functional theory. It is shown that the reactivity of Si(001) is locally enhanced by In adsorption and leads to the formation of one-dimensional In chains. It is demonstrated that the formation of such chains can be described as a two-stage process. In the initial stages of chain formation (≤ 3 In atoms), the binding energy of each additional In atom is strongly dependent on the number of In adatoms, and where they are adsorbed on the surface. The most stable configuration for a single In atom is found to be an end-dimer-bridge monomer structure, while that for two In atoms is the parallel inter-dimer-row (ad-dimer) configuration. In the second stage of chain growth (> 3 In atoms), the binding energy values of the additional In atoms adsorbed on Si(001) are essentially constant. All of the In structures formed in stages one and two which contain In monomers are determined to be metallic, while those consisting of only In-In dimers are semiconducting.

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I. INTRODUCTION

The controlled assembly of adsorbate structures on solid surfaces enables tailoring of the properties of these structures for various specific applications. Of the many different types of assembly processes, self-assembly based on strong adatom-substrate interaction offers a very attractive bottom-up approach for forming regular nanostructures. In this context, the Si(001) surface represents a natural template for the self-assembly of one-dimensional structures (chains) due to the geometrical anisotropy of this surface induced by the surface dimers.

Scanning tunneling microscopy (STM) studies have evidenced the spontaneous growth of In, Al, Ga, Ge, Pb, and Sn chains on the Si(001) surface at room temperature.^{1–6} These self-assembled structures are typical examples of one-dimensional growth based on adatom-substrate-interaction. The chains are observed to form in a direction perpendicular to the dimer rows and are randomly distributed on the substrate. In the case of Al on the Si(001) 2×1 reconstructed surface, the formation of these chains has been described as a surface polymerization reaction with the reactive intermediates having their highest occupied orbital only partially occupied, and being alternately located on the surface and the adatoms.⁷

In this paper we extend earlier theoretical studies of the interaction of Group III atoms with the Si(001) surface^{3,6–11} by performing detailed calculations of the growth of In chains on the reconstructed Si(001) surface. While previous studies have considered different aspects of the interaction of In with the clean Si(001) surface,^{3,8–11} none, to our knowledge, have carried out a systematic study of the progressive formation of In chains on Si(001).

Dai *et al.*^{9,10} showed that In adsorption is more favorable on the reconstructed Si(001) surface than on the ideal (1×1) surface, and that interdiffusion of In into the substrate would not be favorable under equilibrium conditions. In addition, Albao *et al.*¹¹ showed that the barriers for diffusion between preferred In adsorption sites on Si(001) are fairly

small (0.18–0.27 eV). These studies indicate that incident In atoms will remain above the Si(001) surface and readily move to form minimum-energy structures. They thus support the STM observations of the self-assembly of In chains on the clean reconstructed Si(001) surface.^{12,13} Several studies have also shown that In chains readily form on Si(001) surfaces containing imperfections such as C defects.^{5,6}

In order to delineate the mechanisms underlying the growth of In chains on the clean Si(001) reconstructed surface, we have calculated the optimized geometries, energetics, and electronic structure for each successive stage in the chain development from a single adatom, to a chain comprising five In atoms. We have found that the growth process evolves from an initial local activation of the surface, to that which mediates the long-range growth of the chain, and that this involves two distinct steps. In the initial stage, the binding energies of the In atoms chemisorbed on the surface depend on their number and where they are adsorbed. As more In atoms are deposited onto the surface, however, this initial site dependence of the adsorption energy disappears, and the binding energy of each subsequent In atom added to the chain follows a fixed pattern.

The theoretical methods that we have employed are outlined in Sec. II. The results of our study are then presented in Sec. III. The energetics associated with the chain growth is discussed first, followed by a detailed description of the geometries and electronic structures of the lowest-energy configurations corresponding to one to five In atoms. Simulated images that could be compared with experimental STM data are also presented in this section. The main results derived from this work are then summarized in Sec. IV.

II. METHOD

We have performed spin polarized, total energy geometry optimization, and electronic structure calculations based on density functional theory (DFT) using the VASP plane wave method^{14,15} with the PW91 generalized gradient approximation¹⁶ for exchange and correlation and Vanderbilt

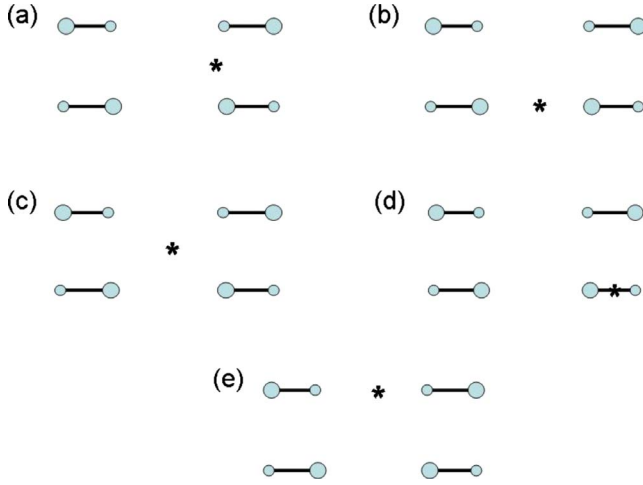


FIG. 1. (Color online) Schematics of the stable structures that result from the adsorption of a single In atom on the Si(001) $c(4 \times 2)$ surface. In this and subsequent figures the larger/smaller circles denote the up/down Si dimer atoms. The Si dimers are indicated by the solid lines and the chemisorbed In atoms by the asterisks.

ultrasoft pseudopotentials.¹⁷ For the Si(001) surface we adopt the ground-state configuration which consists of rows of paired atoms (buckled dimers) forming a $c(4 \times 2)$ reconstruction. The interaction of the In adatoms with this Si(001) $c(4 \times 2)$ surface has been modeled using slabs containing six silicon layers, with 4×4 and 6×4 surface unit cells, and 11 Å of vacuum. The bottom of each slab was terminated by hydrogen atoms. In the total energy minimization calculations the top four layers of the slab and the adsorbed In atoms were allowed to move. The Brillouin zone integrations were performed using four special k points within the irreducible symmetry element.

The binding energy of each In atom added to a chain has been calculated using the formula

$$E_b = E_s[n+1] - E_s[n] - E[\text{In}], \quad (1)$$

where $E_s[n+1]$, $E_s[n]$, and $E[\text{In}]$ are the total energies of a slab with $(n+1)$ In adatoms, a slab with n In atoms, and the energy of an isolated In atom, respectively.

The surface charge density distribution was analyzed by integrating the local density of states (LDOS) from the Fermi energy to either -0.2 eV or -1.0 eV.

Using the above methodology to study the clean Si(001) surface leads to the $c(4 \times 2)$ reconstruction being the preferred structure with the Si-Si surface dimers having a bond length of 2.37 Å and a buckling angle of 18.6°. These values are in excellent agreement with other theoretical values and experiment.¹⁸

III. RESULTS AND DISCUSSION

A. Energetics of the In adatom structures

The most energetically stable geometry for a single In atom chemisorbed on the clean Si(001) $c(4 \times 2)$ surface was

found to be the monomer end-dimer-bridge configuration shown schematically in Fig. 1(a). In this geometry, the In adatom bridges across the ends of two adjacent dimers in the same dimer row. This prediction is in agreement with similar calculations performed for In on Si(001) by Takeuchi.⁸ The binding energy for this end-dimer-bridge adsorption site was calculated to be 2.57 eV, in excellent agreement with the value of 2.56 eV quoted by Kocan *et al.*⁶ It should be noted that the energy of the In-chemisorbed structures are always more negative (i.e., the system is more stable) than the sum of the energies of an isolated In atom, and the chemisorbed system with one less In atom. As a result, the binding energy values given by Eq. (1) are negative. We have followed the standard practice, however, of referring to these as positive numbers.

Two alternate, but less stable, sites result in the inter-row bridging configurations shown in Figs. 1(b) and 1(c). In the structure shown in Fig. 1(b), the In atom sits midway above the line joining two Si-up atoms of dimers on adjacent dimer rows; while in the structure shown in Fig. 1(c), the In adatom is again positioned midway between two dimer rows but has moved toward the Si-down atoms of the neighboring dimers. The In atom binding energies for these two sites [Figs. 1(b) and 1(c)] were found to be smaller than for the end-dimer-bridge configuration [Fig. 1(a)] by 0.17 and 0.09 eV, respectively. All of these configurations retain the original buckling orientations of the Si-Si dimers, although the buckling angles of the chemisorbed dimers are reduced by up to 6° in magnitude.

In addition to the above three sites, we also found stable sites directly on top of a Si-Si dimer [Fig. 1(d)], and midway above the line joining the Si-down atoms of dimers on adjacent dimer rows [Fig. 1(e)], but these have even smaller binding energies. The threefold site between two adjacent dimers of the same dimer row predicted by Takeuchi⁸ was not found to be stable in our VASP calculations.

The adsorption of a second In atom on Si(001) with the most stable monomer configuration [the end-dimer-bridge in Fig. 1(a)] leads to two possible structures—the parallel inter-dimer-row configuration [Fig. 2(b)] and the parallel intra-dimer-row configuration [Fig. 2(g)]. An antiparallel inter-dimer-row structure, which originates from the higher energy monomer structure shown in Fig. 1(e), was also found to be stable. All three of these dimer structures were predicted for the adsorption of Al on Si(001).⁷ The most stable of these structures is the parallel inter-dimer-row configuration [Fig. 2(b)], with the parallel intra-dimer-row configuration [Fig. 2(g)] and the antiparallel structure being 0.24 and 0.39 eV higher in energy, respectively. These results are in good agreement with those of Dai *et al.*⁹ who also found the parallel inter-dimer-row configuration to be the lowest-energy structure for two In atoms, with the other two structures being, respectively, 0.11 and 0.56 eV higher in energy. Dai *et al.* also found a stable antiparallel intra-dimer-row configuration, but its energy was much higher (0.95 eV) than the parallel inter-dimer-row structure. To our knowledge, neither of the antiparallel structures have been observed in experiment, and hence will not be further discussed.

The binding energies of the second In atom for the parallel inter-dimer-row [Fig. 2(b)] and the parallel intra-dimer-

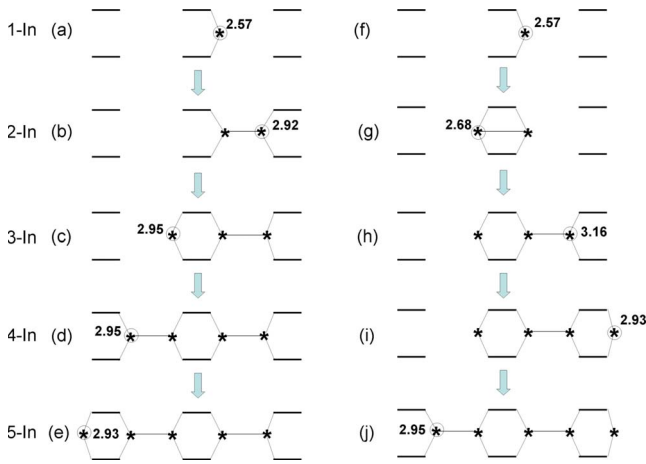


FIG. 2. (Color online) Schematics of two growth processes that result from the successive addition of In atoms to the end-dimer-bridging monomer configuration to create chains perpendicular to the dimer rows. The added In atom in each case is denoted by a circle and its binding energy (in eV) given by the attached numeric. The five-In values are predictions rather than calculated values.

row [Fig. 2(g)] structures were calculated to be 2.92 and 2.68 eV, respectively. These values are higher than the binding energy of the In monomer by 0.35 and 0.11 eV, respectively. This confirms that the formation of either the parallel inter-dimer-row or intra-dimer-row structure is more energetically favorable than the creation of another isolated monomer (with a binding energy of 2.57 eV). It should be noted, however, that our calculated energy gain for the lowest-energy two-In structure, the parallel inter-dimer-row structure, of 0.35 eV is considerably less than the value of 1.0 eV quoted by Takeuchi.⁸

Two possible pathways exist for the formation of a three-In chain structure, but only one three-In configuration is formed [see Figs. 2(c) and 2(h)]. If the third In atom is added to the parallel inter-dimer-row structure to form a finite three-In chain [see Figs. 2(b) and 2(c)], the adsorption energy for this atom is determined to be 2.95 eV. This binding energy is 0.38 eV larger than that for the original monomer (2.57 eV) and in good agreement with the value of 0.40 eV obtained for Al on Si(001).⁷ By contrast, if the third In atom is added to the higher energy parallel intra-dimer-row structure [see Figs. 2(g) and 2(h)], its adsorption energy is calculated to be 3.16 eV, 0.23 eV higher than for a third In atom added to the parallel inter-dimer-row structure.

Adding a fourth In atom to the three-In chain can produce two different four-In chains. If the fourth In atom is adsorbed near the monomer position between bare Si-Si dimers of the adjacent dimer row [see Figs. 2(c) and 2(d)], we obtain the two inter-dimer-row configuration shown in Fig. 2(d). The binding energy for the additional (fourth) In atom in this case is 2.95 eV. If the fourth In atom is chemisorbed at the remaining monomer position of the Si-Si dimers of the three-In structure [see Figs. 2(h) and 2(i)], we obtain the four-In configuration shown in Fig. 2(i). This consists of one inter-dimer-row structure plus two monomers. The binding energy of the fourth In atom for this configuration is 2.93 eV.

It is important to notice that the binding energies corresponding to the fourth In atom being adsorbed at a monomer

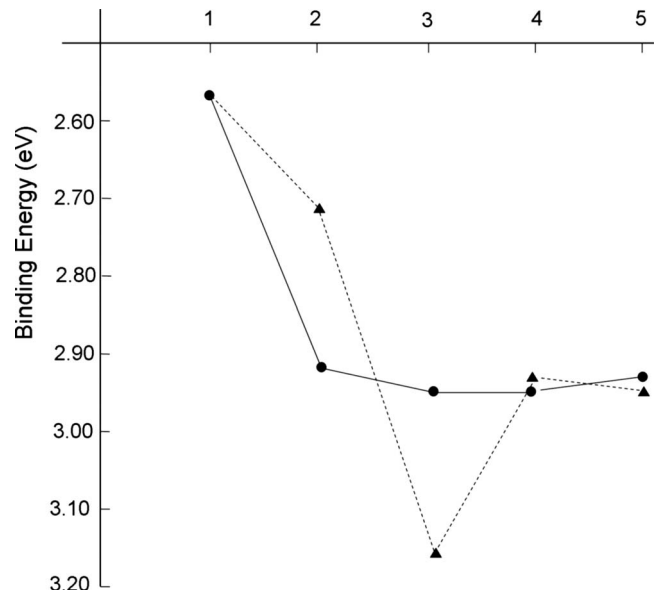


FIG. 3. Variation of the binding energy with the number of In atoms forming the chain. The circles represent the lowest-energy path from the parallel inter-dimer-row configuration. The triangles correspond to the reaction path shown on the right of Fig. 2, which includes the parallel intra-dimer-row structure.

or In-In dimer position are nearly equal (2.93 eV vs 2.95 eV). This is in contrast to the formation of the three-In chain where the adsorption energy for the third In atom at the monomer site is 0.21 eV less than at the In-In interdimer site. This change in behavior defines the two stages of the In chain formation process—the initial chemical functionalization of the surface (one to three In adatoms), and then the chain growth mode (four or more In adatoms). This is clearly seen in Fig. 3 where all of the calculated binding energies are plotted. The data show that for the longer In chains (≥ 4 In atoms) the formation of In-In interdimers is only slightly preferred over the formation of In monomers, whereas for the short In chains the formation of In-In interdimers is noticeably more energetically favorable.

Addition of a fifth In atom on either side of the four-In chains shown in Figs. 2(d) and 2(i) leads to the formation of five-In atom chains, which are identical by mirror symmetry [compare Figs. 2(e) and 2(j)]. Based on our results for three and four In adatoms we would predict the binding energy for the first case [Fig. 2(e)] to be 2.93 eV [the same as going from Fig. 2(h) to Fig. 2(i)], and for the second case [Fig. 2(j)] to be 2.95 eV [the same as going from Fig. 2(c) to Fig. 2(d)]. These predicted binding energies are also plotted in Fig. 3.

B. Activation barriers

As stated earlier, Albao *et al.*¹¹ calculated the potential energy surface for a single In atom on the Si(001) surface and found that the barriers for an In atom to migrate between its different preferred sites were fairly small (0.18–0.27 eV). As a result, we would expect the one-In and two-In configurations shown in Figs. 2(a), 2(b), and 2(g) to readily form at

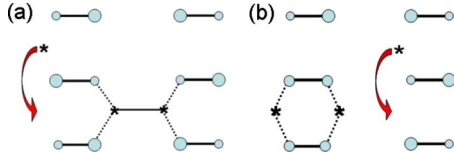


FIG. 4. (Color online) Transition of an In atom at an adjacent end-bridge site to form the three-In configuration shown in Figs. 2(c) and 2(h) from the two-In (a) parallel inter-dimer-row and (b) intra-dimer-row configurations shown in Figs. 2(b) and 2(g).

room temperature. To form a three-In chain, as we have seen, an In atom must either adsorb at an adjacent end-bridge site for the two-In inter-dimer-row configuration [see Figs. 2(b) and 2(c)], or at the end-bridge site of an adjacent dimer [see Figs. 2(g) and 2(h)]. In fact, these same processes define the entire ongoing development of the chain as evidenced by the transitions from Figs. 2(c)–2(e) and 2(h)–2(j).

To calculate the activation barriers associated with these two processes we have employed the nudged elastic band method contained in the VASP code.^{14,15} The two scenarios that we have considered are shown in Fig. 4, and describe the transition of an In atom from an end-bridge site of an adjacent dimer to form the three-In configuration shown in Figs. 2(c) and 2(h). The activation barriers for these two processes were determined to be 0.46 and 0.41 eV, respectively. Given the high mobility of individual In atoms on the Si(001) surface, and the fact that each step of the chain growth process results in a lowering of the total energy of the system, we would thus expect these processes to readily occur at room temperature. The activation energies for a three-In chain to revert back to the original structures shown in Figs. 4(a) and 4(b) were determined to be 0.70 and 1.00 eV, respectively. Since both of these values are significantly greater than the forward activation energies, it follows that the ongoing reaction processes will always be preferred. This is consistent with the spontaneous growth of such chains on Si(001) as evidenced by STM experiments.^{12,13}

C. Geometry and electronic structure of the most stable monomer configuration

The different energetics of the In atoms in stages 1 and 2 of the In chain growth indicates that the bonding configuration of each In atom within a given structure depends on its topology; that is, whether a monomer, a dimer, or a long chain of In atoms is being formed. To clarify this, we now turn to discuss the bonding structure based on the calculated geometries and corresponding electronic structures.

The geometry of the lowest-energy monomer configuration (the end-dimer-bridge structure) is shown in Fig. 5. The two In-Si bond lengths are calculated to be essentially the same (2.80 Å, 2.82 Å) with the adatom located midway between the two Si atoms to which it is bonded, and close to the vertical position. The buckled geometry of the two Si-Si dimers which interact directly with the In atom is retained, with the buckling angles reduced from 18.6° to 15.9° for the dimer bonding to the In via its down-Si atom, and from -18.6° to -12.9° for the up-Si bonding atom. It should be

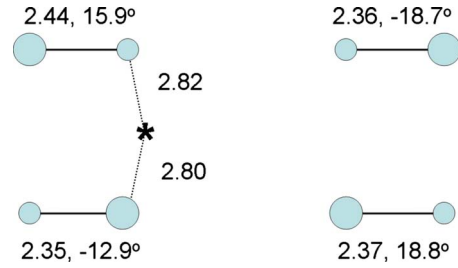


FIG. 5. (Color online) Schematic of the geometry of the end-dimer-bridge monomer structure. The bond lengths are in Å. A positive buckling angle indicates that the atom on the left is higher than that on the right.

noted, however, that while the dimer bond length associated with the bonding Si-up atom (2.35 Å) is close to that on the clean surface (2.37 Å), the dimer bond length of the bonding Si-down atom is elongated to 2.44 Å. Such a geometry implies a very specific interdimer charge redistribution between the Si atoms mediated by the adsorption of In. To further elucidate this, however, we need to calculate the surface electronic structure for this end-dimer-bridge configuration. This is shown in Fig. 6(b), and is metallic. The dispersive band that crosses the Fermi level is similar to the lowest-energy state from the π* unoccupied surface state band of clean Si(001) [see Fig. 6(a)].

To reconcile the geometrical features of the chemisorbed system with its electronic structure, a band resolved partial

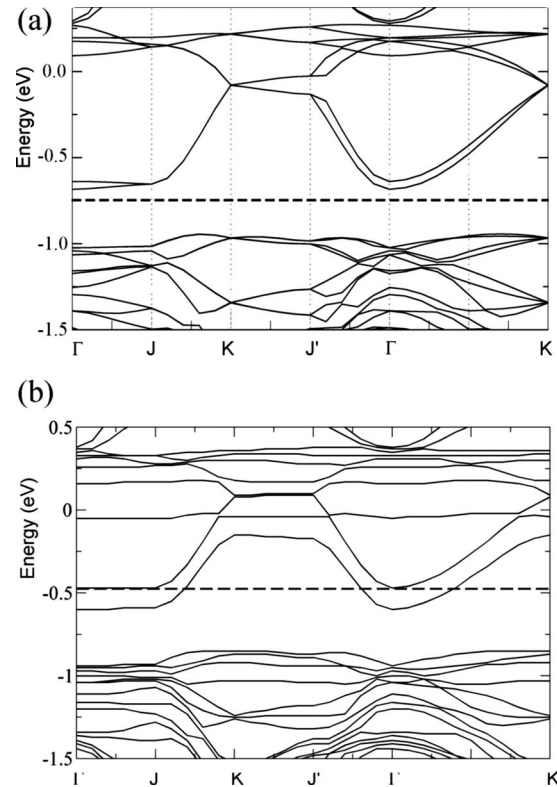


FIG. 6. Electronic structures for the (a) clean Si(001)_c(4 × 2) surface and (b) end-dimer-bridge monomer configuration. The horizontal dashed lines indicate the Fermi energies.

charge density analysis was performed for all of the valence and conduction band states within 1.5 eV of the Fermi energy. In this energy range we have identified four states with bonding structures that contain significant contributions from both the In adatom and the substrate Si atoms.

As In is a trivalent atom, and we have two available surface electrons from the bonding Si-Si dimers (from the bonding up-Si atom), there are five electrons involved in the monomer In-Si(001) interaction. The states involving the two 5s electrons of the In atom were found to lie at the bottom of the valence band, and to be very dispersive. As a result, these states do not form any localized bonding structure. Of the three p orbitals of the In atom, the p_x orbital is empty and does not interact with either of the neighboring dangling bonds, or any other Si atoms. The nominally empty $In p_y$ orbital (which is oriented parallel to the dimer rows), on the other hand, contributes strongly to a very localized shallow band ~ 1.3 eV below the Fermi level. This orbital couples to both the adjacent empty Si-down and filled Si-up dangling bond orbitals and enables the two electrons from the nucleophilic Si-up atom to be shared with the empty dangling bond of the electrophilic Si-down atom. The resultant gain in charge by the Si-down atom explains the increase in its dimer bond length from 2.36 Å to 2.44 Å, and the reduction of its buckling angle from 18.6° to 15.9°. The loss of charge by the Si-up atom of the second dimer involved in the interaction does not alter the bond length of this dimer, which is now charge deficient, but reduces its buckling angle from -18.6° to -12.9° .

The p_z orbital of the In monomer interacts with the nearest second layer Si atom, and also via a π -like interaction, with the empty dangling bonds of the bare Si-Si dimers within the same dimer row. This coupling produces the dispersive state that crosses the Fermi energy. The π -like bonding associated with this state explains its characteristic clean-surface-like dispersion. The fact that this half-occupied state is flat between Γ -J and K-J', but dispersive along J-K and J'- Γ , indicates that the fifth electron involved in the In-surface interaction will be delocalized along the dimer row. This is clearly demonstrated by the -0.2 eV ILDOS plot in Fig. 7, which reflects the spatial charge density distribution of this state. This figure also shows that this partially occupied band is comprised of orbitals associated with both the In adatom and the Si surface atom dangling bonds.

D. Geometries and electronic structures of the parallel inter-dimer-row and intra-dimer-row configurations

As noted earlier, starting with the end-dimer-bridge monomer configuration, and adsorbing a second In atom at the nearest monomer site of the adjacent dimer row, results in the formation of the parallel inter-dimer-row structure [see Figs. 2(a) and 2(b)]. The geometry of this lowest-energy configuration for two In atoms is illustrated in Fig. 8. The In-In distance is 2.99 Å and the In-Si bond lengths are 2.71 Å, 2.72 Å, and 2.78 Å. These values are in reasonably good agreement with the values of 2.70 Å and 2.71 Å determined by Magaud *et al.*³ Our In-In dimer bond length of 2.99 Å is

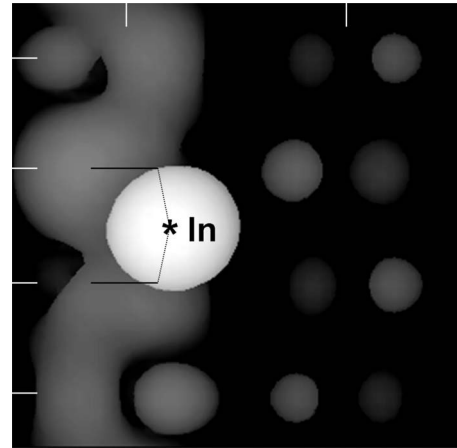


FIG. 7. ILDOS plot for the end-dimer-bridge monomer configuration corresponding to integrating downward from the Fermi level by 0.2 eV. The white vertical and horizontal lines indicate the middle of the dimer rows, and the dimer positions, respectively.

also consistent with their prediction of 2.92 Å. However, we find the Si-Si dimers remain significantly buckled, whereas they predict them to be flat. The In-In and In-Si bond lengths calculated by Takeuchi⁸ for this structure of 2.85 Å and 2.59 Å are significantly different from both our results and those of Magaud *et al.*³

Close inspection of the inter-dimer-row geometry in Fig. 8 reveals important differences in its bonding structure compared with that of the monomer configuration. One observes that the interaction of the In atoms with the Si-up atoms results in the formation of marginally shorter Si-In bonds than for the end-dimer-bridge monomer structure, but does not really affect the buckling angle and bond length of the corresponding Si dimer (see Fig. 5). By contrast, interaction of the In atoms with the Si-down atoms significantly reduces the In-Si bond lengths from 2.82 Å to 2.72 Å, and the buckling angle of the Si dimers from 15.9° to 9.8°. The corresponding In-Si-Si bond angles are also increased from 87.5° for the end-dimer-bridge monomer configuration (Fig. 5) to $\sim 111^\circ$, close to the tetrahedral angle of 109.9°. From the calculated -1.0 eV ILDOS shown in Fig. 9 we observe that the formation of the In-In inter-dimer induces significant charge redistribution between each In atom and its neighboring Si atoms. In particular, there is a noticeable accumulation of charge between the In and Si-down atoms (corresponding

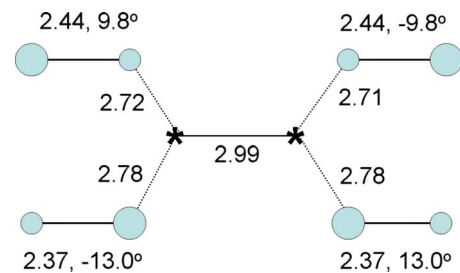


FIG. 8. (Color online) Schematic of the geometry of the parallel inter-dimer-row configuration for two In atoms on Si(001).

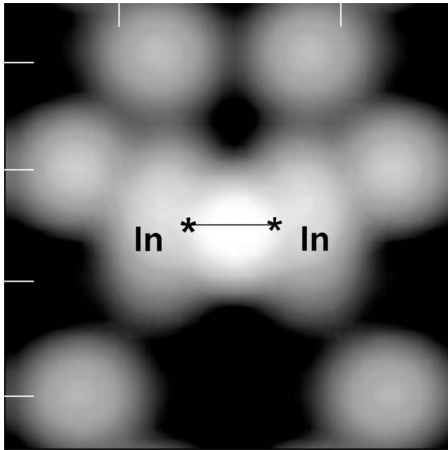


FIG. 9. ILDOS plot for -1.0 eV for the parallel inter-dimer-row configuration.

to the shorter Si-In bonds), and visible charge depletion between the In and Si-up atoms. The In-Si bonds involving these latter atoms are longer (by ~ 0.07 Å) and are similar to those formed in the In monomer configuration [see Fig. 5].

The bonding configuration for the two-In parallel intra-dimer-row structure is shown in Fig. 10 and is substantially different to that for the parallel inter-dimer-row configuration [Fig. 8]. The intra-dimer-row structure results from adsorbing a second In atom at the other monomer site of the end-dimer-bridge configuration and leads to the formation of a flat In-In dimer with an In-In distance of 3.10 Å, 0.11 Å longer than for the inter-dimer-row structure. The In-Si bond lengths have values of 2.76 Å or 2.77 Å, slightly shorter than those of the In monomer [Fig. 5], but longer than the shorter pair of In-Si bonds of the parallel interdimer configuration [Fig. 8]. This suggests that the adsorbed In atoms mediate an interdimer redistribution of the charge between the Si-up and Si-down atoms similar to that observed for the In monomer [Fig. 5]. This charge redistribution between the Si-up and Si-down atoms results in the Si dimers being very flat with buckling angles of $\pm 1.5^\circ$ and bond lengths of 2.41 Å. This is quite different to the preferred clean-surface configuration where the dimers are alternately buckled at $\pm 18.6^\circ$ and have bond lengths of 2.37 Å. In addition, the average In-Si-Si bond angle for this configuration is 97.2° , which deviates from the preferred tetrahedral angle by almost 13° . It thus follows that the In-In intra-dimer-row structure possesses considerable strain. We believe that this is a

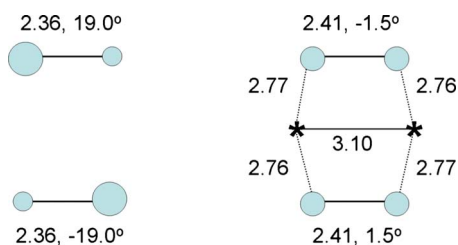


FIG. 10. (Color online) Schematic of the geometry of the parallel intra-dimer-row structure.

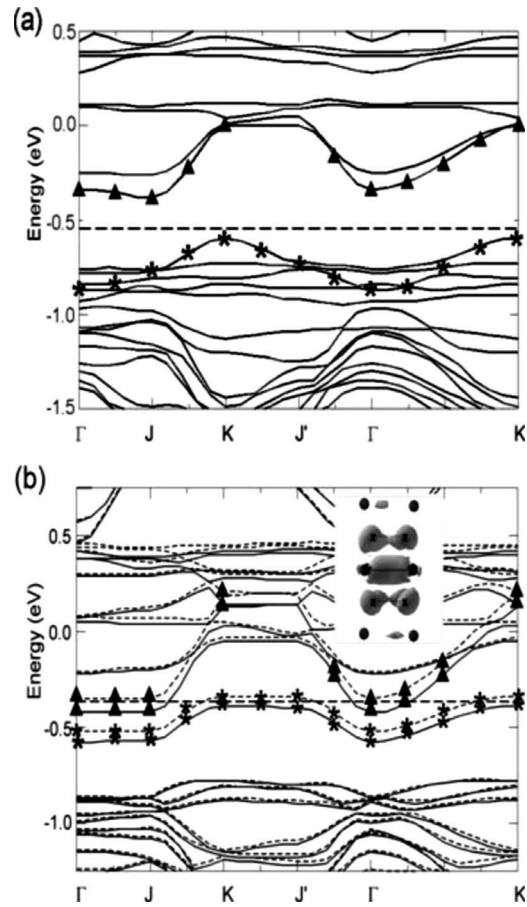


FIG. 11. Electronic structures of the (a) parallel inter-dimer-row and (b) parallel intra-dimer-row configurations. The Fermi levels are indicated by the horizontal dashed lines. The majority and minority spin-split bands in (b) are indicated by the solid and dashed lines, respectively. The two spin-split surface states discussed in the text are indicated by the triangles (\blacktriangle) and asterisks ($*$). The inset shows the charge density distribution for the states represented by the asterisks at the K point. The crosses/asterisks indicate the positions of the neighboring Si dimer atoms and In atoms, respectively. The bold and dotted lines represent the Si-Si and In-In bonds.

primary reason for the parallel intra-dimer-row structure being 0.24 eV less energetically favorable than the parallel inter-dimer-row configuration, despite the fact that in the former structure all of the broken π bonds on the Si dimers are involved in interacting with the In adatoms. Similar energetic ordering was obtained for Al on Si(001) with the parallel inter-dimer-row structure predicted to be 0.25 eV more stable than the parallel intra-dimer-row configuration, and 0.91 eV lower in energy than the antiparallel inter-dimer-row structure.⁷

The electronic structures of the parallel inter-dimer-row and intra-dimer-row structures are shown in Figs. 11(a) and 11(b), respectively. The inter-dimer-row surface electronic structure is semiconducting, while the intra-dimer-row configuration is metallic. For the intra-dimer-row structure we observe, in contrast to the single monomer band structure [see Fig. 6(b)], that there are now two spin-split surface states with their bands either completely or partially below the Fermi level [see Fig. 11(b)]. One of these states (indi-

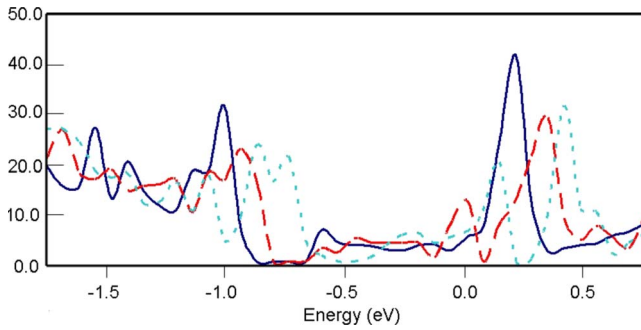


FIG. 12. (Color online) The total electronic density of states (DOS) (in number of states/unit cell) corresponding to the clean Si(001) $c(4 \times 2)$ surface [solid (dark blue) line, $E_F = -0.73$ eV], the one-In end-bridge-dimer configuration [long-dashed (red) line, $E_F = -0.48$ eV], and the two-In inter-dimer-row configuration [short-dashed (light blue) line, $E_F = -0.47$ eV].

cated by the triangles) retains its strongly dispersive nature, similar to the end-dimer-bridge monomer structure, while the second (indicated by the asterisks) is more localized. Band-resolved charge density plots for this latter state show significant overlap between the orbitals of the two In atoms [see the inset in Fig. 11(b)], indicating a long-range bonding interaction between the In monomers forming the two-In intra-dimer-row configuration. It is important to notice, however, that all of the charge of the partially occupied, more-dispersive state is associated with the down-Si atoms of the Si-Si dimers of the neighboring dimer rows. This indicates that some of the charge associated with the two unpaired electrons of the In adatoms becomes delocalized, and is not directly involved in the interaction between the In atoms.

The overall topology of the surface state band structure for the parallel inter-dimer-row structure [Fig. 11(a)] is similar to that for the intra-dimer-row geometry [Fig. 11(b)]. The main differences are that the strongly dispersive state (triangles) becomes unoccupied, while the less dispersive state (asterisks) representing the In-In coupling becomes more dispersive and is now fully occupied (that is, it contains two electrons).

It is also interesting to note that when the parallel inter-dimer-row or intra-dimer-row structures are formed on the Si(001) surface, the In s and p_y bonding remains virtually the same as in the monomer bonding structure. In both cases, however, the p_x orbitals of the In atoms become involved in the formation of a new band in the vicinity of the Fermi level [indicated by the asterisks in Figs. 11(a) and 11(b)], while the p_z orbitals form an empty unoccupied molecular orbital above the Fermi level.

The effect on the electronic structure of adding first one, and then a second, In atom to the clean Si(001) surface is indicated by the total density of state (DOS) plots shown in Fig. 12. In this figure we have plotted the DOS in the vicinity of the Fermi energy for the clean surface, the one-In end-dimer-bridge configuration, and the two-In inter-dimer-row configuration. We observe that the addition of In leads not only to an increase in the Fermi energy, but also substantially modifies the energy distribution of the states, consistent with the changes in the band structures as discussed above.

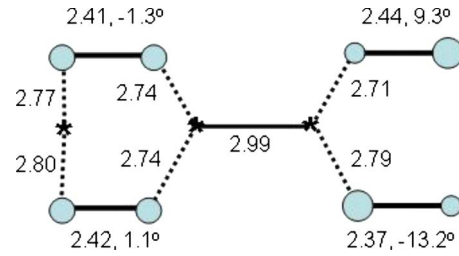


FIG. 13. (Color online) Schematic of the geometry of the three-In configuration derived from the parallel intra- and inter-dimer-row configurations.

E. Geometry and electronic structure of the three-In configuration

As highlighted earlier, the optimized geometry resulting from the addition of a third In atom to the parallel intra-dimer-row configuration is identical to the three-In configuration that originates from the parallel inter-dimer-row structure [see Figs. 2(c) and 2(h)]. The geometry of this three-In structure is shown in Fig. 13. This structure consists of two In atoms in the inter-dimer-row configuration and one In atom in the end-dimer-bridge monomer geometry.

The In atom on the left of Fig. 13 behaves very similarly to that of a single monomer (see Fig. 5) and sits essentially in a vertical position midway between its two bonding Si dimer atoms with In-Si bond lengths of 2.77 Å and 2.80 Å. The other two In atoms form what is essentially the parallel inter-dimer-row structure with the In-In dimer bond length of 2.99 Å being identical to that of the isolated dimer (see Fig. 8). The remaining In-In distance is 3.47 Å, which is considerably longer than for the parallel intra-dimer-row configuration (3.10 Å). The Si-Si dimers which bond to the monomer In atom have bond lengths of 2.41 Å and 2.42 Å, and buckling angles of -1.3° and 1.1° , respectively. They thus exhibit very similar behavior to the bonding Si-Si dimers of the parallel intra-dimer-row configuration (see Fig. 10). The Si-Si dimers bonded to the In adatom on the right, however, have bond lengths of 2.44 Å and 2.37 Å, and buckling angles of 9.3° and -13.2° , respectively, which match very closely those of the parallel inter-dimer-row structure (see Fig. 8). These results indicate that the charge redistribution and resultant bonding structure of the three-In chain is essentially a combination of the individual In monomer and two-In inter-dimer-row configurations.

Calculations of the electronic structure also support this picture. The electronic band structure for our three-In chain is shown in Fig. 14 and is metallic. Band-resolved charge density analysis shows that the overall topology of this surface state band structure is a mixture of that for the monomer [Fig. 6(b)] and inter-dimer-row [Fig. 11(a)] configurations. The state representing the In-In coupling (see asterisks), for example, is doubly occupied, as for the inter-dimer-row structure, while as for the monomer structure, the dispersive band that crosses the Fermi level originates from coupling between the Si π^* band and the p_z orbital of the In atom in the monomer position.

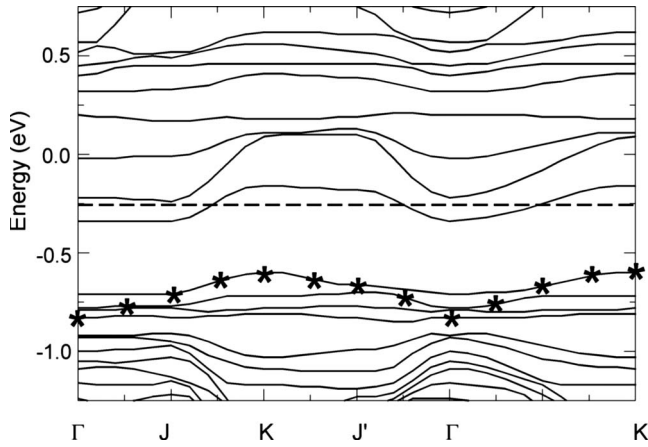


FIG. 14. Electronic structure for the three-In configuration shown in Fig. 13. The asterisks indicate the state arising from strong In-In coupling.

As discussed in (i), if a third In atom is added to the parallel inter-dimer-row structure to form a finite three-In chain [see Figs. 2(b) and 2(c)], the adsorption energy for this atom is 2.95 eV. This value is 0.38 eV larger than that for the original monomer (2.57 eV) and is believed to be due to the fact that adsorption at the new site does not require the breaking of any Si-Si π bonds.⁷ By contrast, if the third In atom is added to the higher energy, highly strained parallel intra-dimer-row configuration [see Figs. 2(g) and 2(h)], its adsorption energy is 3.16 eV, 0.21 eV higher than for a third In atom added to the parallel inter-dimer-row structure. This large value is due to the transformation of the intradimer In-In bond into an interdimer In-In bond, with an associated reduction in the Si-Si-In bond angle strains, as compared to the formation of the same three-In structure from the significantly less strained two-In inter-dimer-row configuration of Fig. 8.

ILDOS plots for our three-In configuration for -1.0 eV and $+1.0$ eV are shown in Fig. 15. According to the Tersoff-

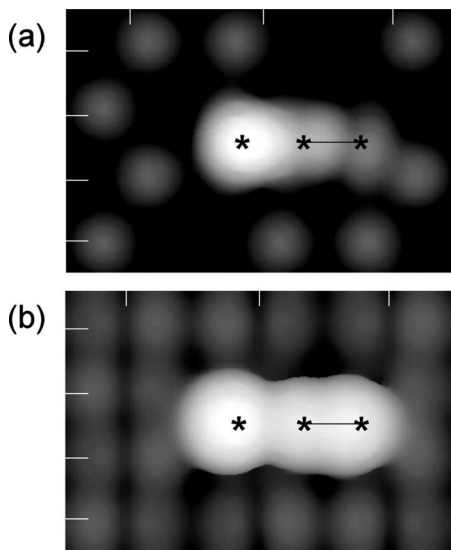


FIG. 15. ILDOS plot for (a) -1.0 eV, and (b) $+1.0$ eV, for the parallel three-In chain configuration that consists of one In dimer and one In monomer.

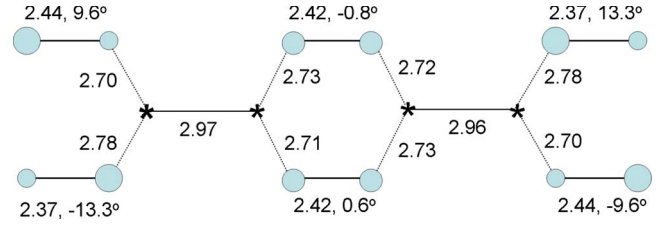


FIG. 16. (Color online) Schematic of the geometry of the four-In chain structure that corresponds to two inter-dimer-row configurations [Fig. 2(d)].

Hamann theory of STM (Ref. 19), these plots can be compared with the filled- and empty-state experimental STM images, respectively. We see from Fig. 15(a) that there is a significant difference in the brightness of an In dimer and monomer termination in filled-state STM images, with the monomer site being brighter. However, no significant difference between these two sites is observed in the empty-state image [$+1.0$ eV ILDOS in Fig. 15(b)]. These features are also clearly seen for the four-In chain structure shown in Fig. 18 (see the ILDOS in Fig. 19). They are also in agreement with the experimental STM images of Kocan *et al.*⁵

F. Geometries and electronic structures of the four-In configurations

As noted earlier, adsorbing a fourth In atom at one of the neighboring monomer sites of the three-In configuration shown in Fig. 13 leads to two different four-In structures [see Fig. 2]. The detailed geometry of the first of these four-In chains is presented in Fig. 16. The central Si-Si dimers surrounded by the In-In interdimerers are almost flat and have a bond length of 2.42 \AA , close to that of the chemisorbed dimers of the parallel intra-dimer-row configuration [see Fig. 10]. All four Si-In bonds are between 2.71 – 2.73 \AA , similar to the short Si-In bonds in the parallel inter-dimer-row structure. The In-In bond lengths are 2.96 \AA and 2.97 \AA , only slightly shorter than that for the two-In parallel inter-dimer-row configuration [see Fig. 8]. These similarities are reflected in the calculated charge density plot shown in Fig. 17(a). We observe a symmetric charge density distribution between the In atoms and the central Si-Si dimer atoms, which is characteristic of the shorter Si-In bonds. By contrast, the Si-In bond lengths and the associated charge distribution, as well as the bond lengths and buckling angles of the “end” Si-Si dimers, are virtually identical to those in the two-In parallel inter-dimer-row configuration and the three-In chain (see Figs. 8 and 13, respectively). Looking at the ILDOS plots in Fig. 17 as simulated STM images, we can conclude that the In-In dimers will be imaged more brightly in filled state than the surrounding bare Si-Si dimers [Fig. 17(a)]. Moreover, the In row will be imaged with higher intensity in empty-state images, than in filled-state images [compare Figs. 17(a) and 17(b)], consistent with experiment.⁵

The geometry of the second four-In chain is shown in Fig. 18. In this case, all of the bonding Si-Si dimers are saturated, and hence these dimers are virtually flat and somewhat

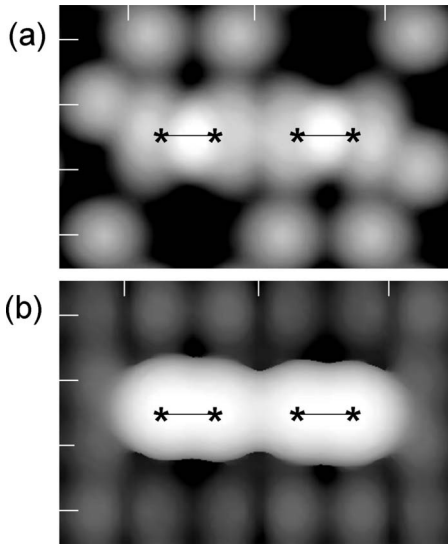


FIG. 17. ILDOS plot for (a) -1.0 eV, and (b) $+1.0$ eV, for the parallel four-In chain configuration that consists of two In-In interdimers.

longer than for the clean surface. The bond length of the In-In inter-dimer is 3.02 \AA , slightly longer than for the other structures. The geometry of each “end group” is seen to be essentially the same as that for the two-In parallel intra-dimer-row structure (see Fig. 10).

The corresponding ILDOS plots for the four-In chain of Fig. 18 are presented in Figs. 19(a) and 19(b). The monomer terminations are observed to image very brightly in filled state, while the In-In dimer has a comparable intensity to the bare Si-Si dimers [see Fig. 19(a)]. However, as noted previously for the three-In configuration, no significant difference between the monomer and In-dimer terminations is observed in the empty-state images [see Fig. 19(b)].

The electronic structure calculations predict that the four-In structure consisting of one In interdimer and two monomers [Fig. 18] is metallic, while that consisting of two In interdimers [Fig. 16] is semiconducting. This is consistent with the general trend that chains containing monomers yield metallic band structures while those containing only In interdimers are semiconducting.

Our calculations predict that the binding energies for the additional (fourth) In atom needed to form these four-In chains are nearly equal [see Figs. 2(d) and 2(i)]. This is due to the fact that these two four-In structures are almost degenerate in energy. This is in striking contrast to the different

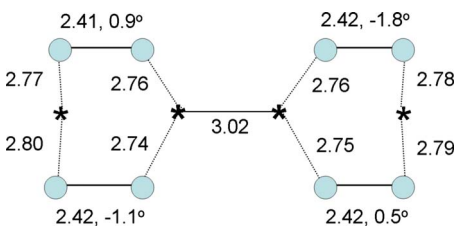


FIG. 18. (Color online) Schematic of the geometry of the four-In chain structure that corresponds to an inter-dimer-row configuration and two monomers [Fig. 2(i)].

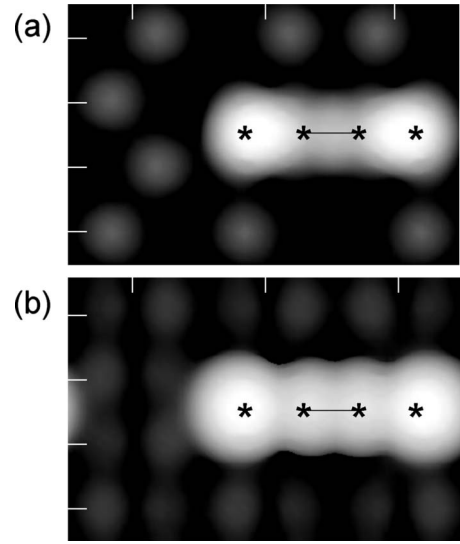


FIG. 19. ILDOS plot for (a) -1.0 eV, and (b) $+1.0$ eV, for the parallel four-In chain configuration that consists of two In monomers and one In dimer (see Fig. 16).

binding energies involved in forming chains containing two and three In atoms [see Fig. 3].

This significant difference in behavior can be explained by analyzing the strain induced in the chains formed from an even number of In adatoms. The difference in energy between the parallel inter- and intra-dimer-row two-In chains comes from the strain inherent in the intra-dimer-row structure of Fig. 10 (where the strain results from the symmetric Si-Si dimers and nonideal In-Si-Si bond angles). This strain is reduced, however, in the process of forming the four-In structure shown in Fig. 18 by the creation of an In interdimer bond. By contrast, the energy gained by the formation of a second In interdimer to produce the four-In structure shown in Fig. 16 is counteracted by the formation of the highly strained central Si-Si dimers. We believe that it is these competing effects which result in the total energies of the two four-In configurations being nearly the same.

IV. SUMMARY

We have shown that In chains on a clean Si(001) surface with asymmetric Si dimers and $c(4 \times 2)$ periodicity result from each successive In atom adsorbing at a reactive site above the surface to form either a new monomer or an In interdimer. Both sites are more reactive (as measured by the binding energy of each additional In adatom added to the existing chain structure) than the respective clean-surface sites. Our calculations have also shown that these two sites produce quite different electronic structures with a chain containing only In interdimers being semiconducting, while those containing monomers are metallic. This is in contrast to the results discussed by Brocks *et al.*⁷ for the chemisorption of Al on clean Si(001). These authors described the formation of Al chains on a Si(001) 2×1 surface as a progressive surface polymerization reaction involving alternating adatom-located monomer and substrate-located reactive sites

with both constituting radicals with a partially occupied state.

We have also shown that the formation of a chain of In atoms on Si(001) involves a two-stage process, with the initial stage corresponding to the formation of chains containing one to three In atoms. For two In atoms, the parallel inter-dimer-row structure was found to be 0.24 eV more stable than the parallel intra-dimer-row structure. The addition of a third In atom to either the parallel inter-dimer-row structure or the intra-dimer-row structure gives rise to the same three-In configuration with the binding energy of the third atoms being 2.92 and 3.16 eV, respectively.

The beginning of the second stage of the chain growth process corresponds to adding a fourth In atom to the three-In configuration. In this stage, there are two possible configurations for each even number of In atoms, but only one configuration for each odd number of adatoms. The binding energy of each additional adatom for this latter part of the chain growth process is essentially constant.

Finally, we have shown that In atoms adsorbed on Si(001) mediate a very specific interdimer charge redistribution between the electron-rich Si-up and electron-deficient Si-down atoms of the Si dimers, to which the In adatoms are bonded. Initially this charge transfer leads to the formation of long In-Si bonds, which are gradually transformed into shorter In-Si bonds at higher In coverage. This process is complete for Si-Si dimers surrounded by In-In interdimer structures, characteristic of long In chains formed on the Si(001) substrate.

ACKNOWLEDGMENTS

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¹J. Nogami, in *Self Assembled Single Atom Wide Metal Lines on Si(100) Surfaces*, edited by C. Joachim and S. Roth, NATO Advanced Research Workshop Series, Atomic and Molecular Wires (Kluwer, Dordrecht, 1997), Vol. 341, pp. 11–21.

²M. M. R. Evans and J. Nogami, *Phys. Rev. B* **59**, 7644 (1999).

³L. Magaud, A. Pasturel, L. Jure, P. Mallet, and J. Y. Veuillen, *Surf. Sci.* **454-456**, 489 (2000).

⁴M. A. Albao, M. M. R. Evans, J. Nogami, D. Zorn, M. S. Gordon, and J. W. Evans, *Phys. Rev. B* **74**, 037402 (2006).

⁵P. Kocan, P. Sobotik, I. Ost'adal, J. Javorsky, and M. Stevin, *Surf. Sci.* **601**, 4506 (2007).

⁶P. Kocán, L. Jurczyk, P. Sobotik, and I. Ost'adal, *Phys. Rev. B* **77**, 113301 (2008).

⁷G. Brocks, P. J. Kelly, and R. Car, *Phys. Rev. Lett.* **70**, 2786 (1993).

⁸N. Takeuchi, *Phys. Rev. B* **63**, 035311 (2000).

⁹X.-Q. Dai, W.-W. Ju, G.-T. Wang, and M. H. Xie, *Surf. Sci.* **572**, 77 (2004).

¹⁰X.-Q. Dai, W.-W. Ju, M. H. Xie, and S. Y. Tong, *Surf. Rev. Lett.* **12**, 483 (2005).

¹¹M. A. Albao, J. W. Evans, and F.-C. Chuang, *J. Phys.: Condens. Matter* **21**, 405002 (2009).

¹²Z.-C. Dong, D. Fujita, and H. Nejoh, *Phys. Rev. B* **63**, 115402 (2001).

¹³J.-L. Li, X. J. Liang, J.-F. Jia, X. Liu, J.-Z. Wang, E.-G. Wang, and Q.-K. Xue, *Appl. Phys. Lett.* **79**, 2826 (2001).

¹⁴G. Kresse and J. Furthmuller, *Comput. Mater. Sci.* **6**, 15 (1996).

¹⁵G. Kresse and J. Furthmuller, *Phys. Rev. B* **54**, 11169 (1996).

¹⁶J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).

¹⁷D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).

¹⁸A. Ramstad, G. Brocks, and P. J. Kelly, *Phys. Rev. B* **51**, 14504 (1995).

¹⁹J. Tersoff and D. R. Hamman, *Phys. Rev. B* **31**, 805 (1985).