

Substrate effects on electronic properties of atomic chains

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A substrate for future atomic chain electronics, where adatoms are placed at designated positions and form atomically precise device components, is studied theoretically. The substrate has to serve as a two-dimensional template for adatom mounting with a reasonable confinement barrier and also provide electronic isolation, preventing unwanted coupling between independent adatom chains. For excellent structural stability, we demand chemical bonding between the adatoms and substrate atoms to secure the positions (chemical bonding scheme), but then good electronic isolation is not always guaranteed and necessary conditions are clarified. The substrate influences fundamental chain properties through chemical bonds. A chain with group IV adatoms having two chemical bonds each, or a chain with group III adatoms having one chemical bond each, is semiconducting. Charge transfer from or to the substrate across the chemical bonds brings about unintentional doping for semiconducting chains. The electronic properties have to be considered for the combination of the adatom and substrate systems in this scheme, even though the adatom modes are well localized in the adatom chains. © 1999 American Vacuum Society. [S0734-2101(99)01304-4]

I. INTRODUCTION

When the semiconductor device size is reduced to 0.07 μm , the number of dopant atoms in the channel is no longer macroscopic, typically less than a hundred.¹⁻³ A spatial distribution of these dopant atoms fluctuates statistically from device to device even in identically designed, fabricated devices, and this places a serious limitation for integration. It may be possible to control dopant positions to some extent,³ but an ultimate control with atomic precision might be difficult. One fundamental solution to this problem is to create electronics that are atomically precise, ordered, but preferably simple. Atomic chains, which are precise structures of adatoms placed on an atomically regulated surface using atom manipulation technology,⁴ are candidates for building components in future electronics. All the adatoms will be placed at designated positions on the substrate, and all the device structures are precise, free from any statistical deviations.

There are two possible schemes to mount adatoms on a substrate surface. For excellent electronic isolation between the adatom and substrate systems, we may forbid chemical bonding between the two systems so that electrons are localized in the adatom system. Then the adatoms will have to be confined by the van der Waals interaction, but it is usually too weak to provide satisfactory confinement even at low temperatures.⁵ For excellent structural stability, we may in turn allow chemical bonding so that the adatoms are not displaced with thermal agitation from their ideal positions, but this scheme may suffer unwanted substrate effects of poor isolation. In the worst scenario, the electron wave function penetrates deep into the substrate, resulting in crosstalk between chains, which is fatal for electronics applications.

In this article, the latter chemical bonding scheme is studied in detail. We clarify the necessary conditions for the

adatom modes to be localized at the surface, using a one-dimensional tight-binding model in Sec. II. The substrate influences, through chemical bonding, the fundamental properties of adatom chains such as whether they are metallic or semiconducting, and this is explained based on a tight-binding picture in Sec. III. The band structure of semiconducting Ge-adatom chains realized on a Si(100) surface, where unused Si dangling bonds are saturated with H atoms, is studied with a self-consistent tight-binding method, and unintentional doping is predicted due to the charge transfer from and to the substrate. A summary is given in Sec. IV.

II. CONDITIONS FOR EDGE LOCALIZATION AND ELECTRONIC ISOLATION

Electronic isolation can be achieved when an electron wave function is localized at the surface and decays exponentially into the substrate. Therefore, finding electronic isolation conditions can be reduced to finding localization conditions. In order to study the qualitative aspect of localization, finite-length atomic chains are analyzed using a tight-binding method with universal parameters.⁶ We imagine that the substrate is made by grouping atomic chains in bundle as in an inset in Fig. 1, where the chain edges form the top and bottom surfaces. In an atom of each chain, two orbitals along the chain provide a physical mechanism for the exponential decay of the wave function leading to surface (edge) states, while remaining two simply create chemical bonding to other neighboring chains and do not contribute to the localization. Thus, the former two orbitals are included in the current model while the later two are not, and this reflects that the chains are grouped to form a three-dimensional substrate, in contrast to the previous chain models with four orbitals in Ref. 9 used for different purposes. Full multidimensional modeling is not quite rewarding since the decay is essentially a one-dimensional phenomenon perpendicular to the substrate that has to be supported by many lattice peri-

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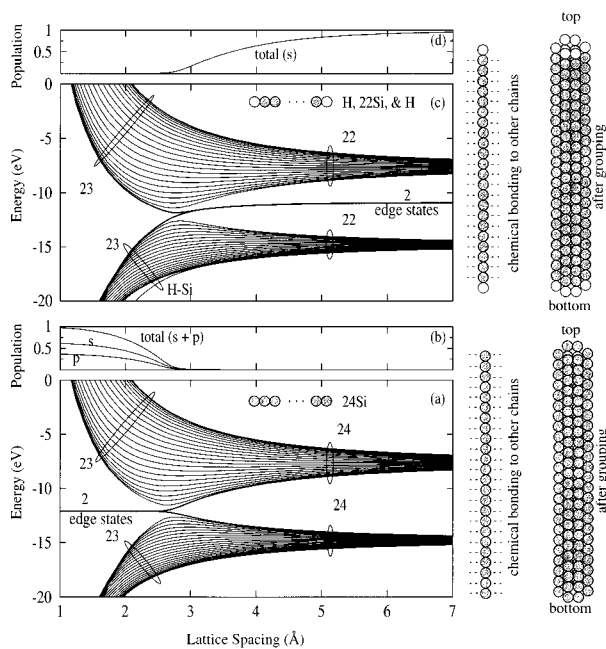


FIG. 1. Edge states as a function of lattice spacing: (a) energy levels and (b) population at edge atoms for band gap modes (thick line) in 24 Si chain; (c) and (d) the same plots in 22 Si chain with two edge H atoms. The number of states is indicated in (a) and (c), and s - and p -orbital contributions are separately shown in (b) and (d). The inset shows the model schematically.

ods. Typically more than fifteen periods are necessary to have results independent of the number of periods, but such many periods are not easily treated in multidimensional modeling.

Figure 1(a) shows the energy levels and 1(b) the electron existence probability at the edge atoms for a chain of 24 Si atoms; 1(c) and 1(d) are the same set of plots for a chain of 22 Si atoms with a H atom placed at each edge, as a function of the lattice spacing. By changing it from infinity to a finite value as a gedanken experiment,⁷ it is shown that how edge states arise from isolated atomic states. $3s$ and parallel $3p$ orbitals represent symmetric and antisymmetric bases in the chain direction, respectively, and are considered in the model. Other two perpendicular $3p$ orbitals are used for chemical bonding with other chains and not considered. General linear combinations of s and p orbitals reflecting more realistic crystal symmetry for the substrate can be taken as bases, but the difference can be absorbed in the redefinition of tight-binding parameters, and there is no change in the qualitative conclusions. In the unsaturated Si chain in Fig. 1(a), the $3s$ -originated filled (valence) band and the $3p$ -originated empty (conduction) band become wider as the lattice spacing is reduced. Around 2.7 \AA , there is an s - p band crossing, where $3s$ - and $3p$ -originated bands cross. For shorter lattice spacing, a new band gap opens, and there appear two edge states, one from the top of the valence band and the other from the bottom of the conduction band. Since they are located inside the band gap, they are strong mixtures of s and p orbitals and are mostly located at the edge atoms as in Fig. 1(b). All the other states are of the penetrating type, spreading over the entire system. Edge states can be

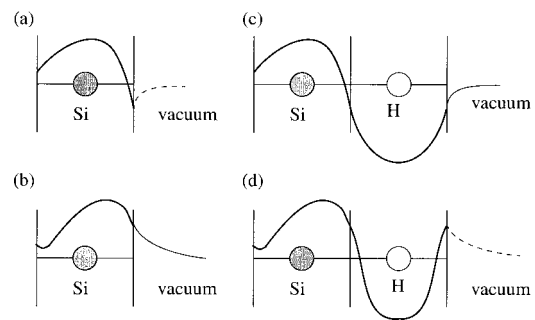


FIG. 2. Schematic plots for envelope shapes of wave functions at vacuum boundary, where unit cells are scaled to be of the same size. For unsaturated chain, (a) long lattice spacing without edge states (forbidden) and (b) short lattice spacing with edge state (allowed) are shown. For H-saturated chain, (c) long lattice spacing with edge states (allowed) and (d) short lattice spacing without edge states (forbidden) are shown.

manipulated with H atoms.⁸ In the H-saturated chain, the edge states appear with s - p uncrossing lattice spacing longer than the crossing point, and disappear with s - p crossing, shorter lattice spacing as in Figs. 1(c) and 1(d).

This complementary behavior can be interpreted based on the Wigner-Seitz picture.⁷ Figure 2 is a set of schematic plots of an envelope for an edge-state wave function near the vacuum boundary. In the unsaturated chain with s - p uncrossing spacing in Fig. 2(a), the wave function has a notch at the vacuum boundary and cannot smoothly connect to the vacuum. Tuning the electron energy does not help since it can change only the gradient of the wave function, but not its sign, and it is impossible to achieve smooth connection. With s - p crossing spacing, the smooth connection is possible this time since the wave function has an opposite sign at the vacuum boundary as in Fig. 2(b). Narrower unit cells are stretched for clarity. In the H-saturated case, the role of the additional H cell is to flip the gradient without changing the functional value. This is possible since a H atom has only one relevant orbital, $1s$, which is symmetric in the unit cell. Because of this gradient flip, the edge states exist with s - p uncrossing spacing as in Fig. 2(c) and disappear with s - p crossing spacing as in Fig. 2(d), and this explains the complementary behavior.

Examples of s - p crossing substrates are semiconducting crystals Si, Ge, or GaAs, and many metallic crystals. S - p uncrossing substrates are alkali halides, such as KCl or LiF. On an s - p crossing substrate, the dangling bonds are where electrons are localized, and if saturated with H atoms, these localized states are eliminated. Oppositely on an s - p uncrossing substrate, H-saturated sites are where electrons are localized, and if H atoms are removed, these localized states are eliminated. For electronic applications, the *absence* of H atoms on an s - p crossing substrate, or the *presence* of H atoms on an s - p uncrossing substrate provides an area with surface-localized electrons, which can be regarded as an active device area.

Figure 3 depicts how the electronic states of an adatom arise in the chemical bonding scheme with a tight-binding picture. There are two ways to obtain a semiconducting

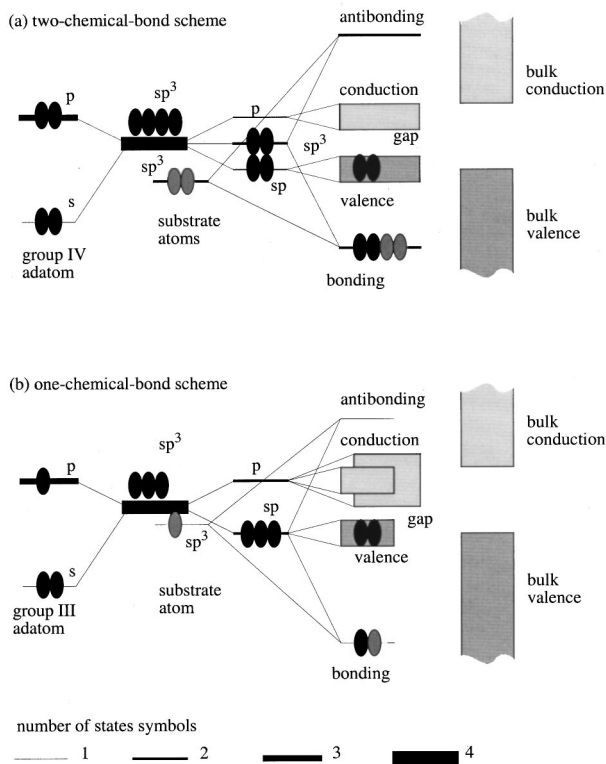


FIG. 3. Tight-binding view for semiconducting adatom chains in the chemical-bonding scheme: (a) group IV adatom with two chemical bonds and (b) group III adatom with one chemical bond. Oval dots are electrons and the number of states are indicated with thickness of lines.

chain: (a) use group IV adatoms with two chemical bonds each, or (b) use group III adatoms with one chemical bond each. Two- and one-chemical-bond schemes are possible, for example, on unreconstructed Si(100) and (111) surfaces, respectively. In a group IV adatom, one s and three p orbitals are rehybridized to form four sp^3 orbitals as in Fig. 3(a). We require that two sp^3 orbitals be used to form two chemical bonds with the substrate atoms. When an orbital from the adatom and another orbital from the substrate atom meet, they form bonding and antibonding orbitals, separated by double the covalent energy (typically several eV).⁶ Two electrons, one from the adatom and the other from the substrate atom, occupy the bonding orbital completely and create a covalent bond. Because of the large covalent energy, the bonding orbital has a very low energy and does not contribute to the adatom properties directly. Since there are two chemical bonds, two adatom electrons are wasted. The remaining two adatom sp^3 orbitals are then rehybridized and form an sp orbital and a p orbital, where the sp orbital is completely filled with remaining two adatom electrons. After the formation of a chain structure, the sp and p orbitals will become valence and conduction bands, respectively. The situation is similar for a group III adatom in Fig. 3(b). The only difference is that after the sp^3 hybridization, orbitals are rehybridized to form two sp orbitals and two p orbitals. One sp orbital is used for a covalent bond with a substrate atom, and therefore one adatom electron is wasted. The other sp orbital is fully filled with two adatom electrons and two p

orbitals are empty. Thus, this sp orbital forms a valence band, and two p orbitals form two conduction bands. Adatom bands can be calculated with a self-consistent tight-binding method based on this picture. With a similar argument, a chain with group II adatoms with no chemical bonds is semiconducting, and this is consistent with the previous results.⁹

Although the edge states for a single adatom has an energy level inside the bulk band gap on an s - p crossing substrate as discussed above, the entire adatom bands are not necessarily included in the bulk band gap. Generally, they may be beyond the band gap. For electronics applications, this is not plausible, but not fatal, either. There has been an experiment observing such surface and bulk states in the current-voltage characteristics of scanning tunneling microscopy for Si(111).¹⁰ The normalized conductance plot as a function of voltage showed five peaks, four attributed to the surface states and one to the bulk states, where the peak positions were consistent with a model assuming *unperturbed* surface and bulk states. We can argue that the coupling was so weak that no significant modulation in peak positions resulted, although this did not directly clarify what happened for electronic isolation between the surface and bulk states in the context of unwanted crosstalk raised above. In the following, we assume that this coupling is small enough, but this problem has to be studied in more detail in the future.

III. ADATOM BANDS WITH SELF-CONSISTENT TIGHT BINDING

We study the band structures of a Ge adatom chain on Si(100), where unused dangling bonds are saturated with H atoms as shown in Fig. 4. Such a hydrogenated Si surface is quite stable.¹¹ According to the tight-binding picture above, this chain is semiconducting, and the wave function is localized at the chain with dangling bonds, not in the hydrogenated area. Since Ge atomic levels are quite close to those of a Si atom, the edge states are localized well at the surface, whose energies are deep inside the bulk Si band gap. Contrary to this, if the adatom levels are quite different from those of substrate atoms, electrons will not be easily localized on an s - p crossing substrate.⁵ We note that there are two kinds of adatom chains with the same lattice spacing, σ and π chains as in Fig. 4, depending on how the covalent bonds align with respect to the chain direction. The resultant band structures are qualitatively different as we shall see.

We first discuss the charge transfer in the σ chain. An adatom (Ge) is 0, two nearest neighbors (Si) are 1, and two second nearest neighbors (H) are 2, where last two neighbors belong to the substrate. Charges are assumed to be distributed up to these second nearest neighbors, and therefore charge neutrality holds within this range. Charge z_i indicates the amount of excess electrons on atom i , and reflects the wave function amplitudes. Thus, z_i 's are determined by the tight-binding parameters, diagonal elements ϵ_i 's, and off-diagonal elements V 's. In turn, these tight-binding parameters are functions of charge amounts z_i 's through the Coulomb interaction, and have to be determined self

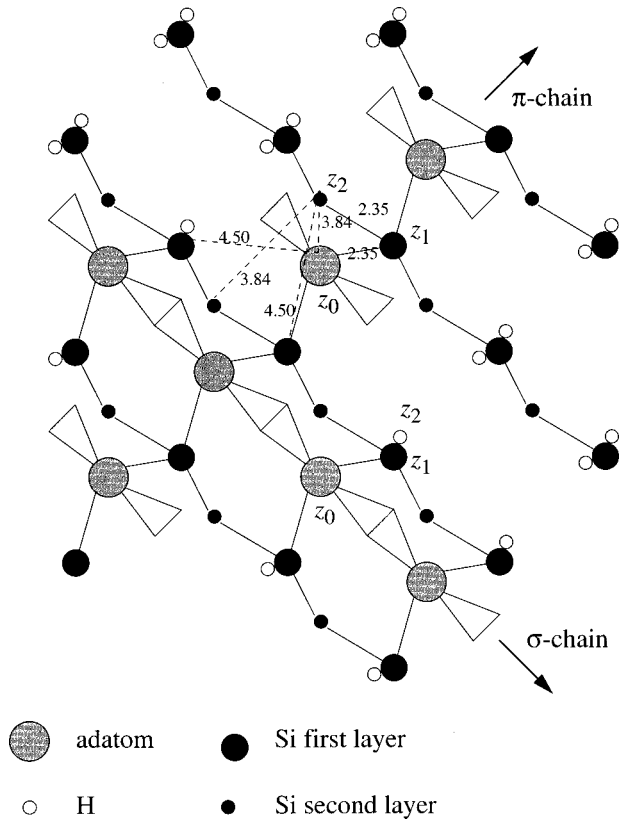


FIG. 4. Adatom σ and π chains on hydrogenated Si(100) surface with adatom charge z_0 , nearest neighbor charge z_1 , and second nearest neighbor charge z_2 . Adatom dangling bonds before rehybridization is shown for clarity, and the distances are indicated in Å.

consistently.¹² As usual, the Coulomb interaction is assumed to change diagonals from $\varepsilon_i^{\text{orig}}$'s, equivalent to atomic term values,⁶ to ε_i 's, but not off-diagonals V 's. Using a bond-orbital approximation introducing the simplest off-diagonal parametrization⁶ and appropriate linearization,¹² we express this self-consistency by the following six equations for six unknowns ε_0 , ε_1 , ε_2 , z_0 , z_1 , and z_2 :

$$z_0 = (\varepsilon_1 - \varepsilon_0) / V_{01}, \quad (1)$$

$$z_1 = (\varepsilon_0 - \varepsilon_1) / 2V_{01} + (\varepsilon_2 - \varepsilon_1) / 2V_{12}, \quad (2)$$

$$z_2 = (\varepsilon_1 - \varepsilon_2) / 2V_{12}, \quad (3)$$

$$\varepsilon_i = \varepsilon_i^{\text{orig}} + c_{i0}z_0 + c_{i1}z_1 + c_{i2}z_2, \quad (i=0, 1, \&2), \quad (4)$$

where V_{01} is an off-diagonal element, the covalent energy for atoms 0 and 1, and V_{12} is the same for atoms 1 and 2. Equations (1)–(3) show how the tight-binding parameters determine the charges (wave functions). A charge conservation relation of $z_0 + 2z_1 + 2z_2 = 0$ automatically holds in this formalism. Equations (4) show how the charges modify the diagonal tight-binding parameters. c_{ij} stands for a coefficient of the Coulomb interaction for atom i due to charge z_j . Coulomb interaction is due to intra-atomic (self-charging) repulsion, interatomic repulsion from the same unit cell, and Madelung interaction from the other unit cells. The Madelung energies are evaluated numerically, expressed as a func-

tion of z_1 and z_2 using the charge conservation relation, and normalized to $W = e^2/3.84$. Each c_{ij} is given by

$$\begin{aligned} c_{00} &= U_0, \\ c_{01} &= 2e^2/2.35 - 0.732W, \\ c_{02} &= 2e^2/3.17 - 1.17W, \\ c_{10} &= e^2/2.35, \\ c_{11} &= U_1 + e^2/3.84 - 0.00644W, \\ c_{12} &= e^2/5.12 + e^2/1.48 - 1.05W, \\ c_{20} &= e^2/3.17, \\ c_{21} &= e^2/5.12 + e^2/1.48 - 0.177W, \\ c_{22} &= U_2 + e^2/6.26 - 0.382W, \end{aligned} \quad (5)$$

where U_i is a self-charging energy for atom i . For example, c_{00} corresponds to a Coulomb energy shift for atom 0 due to its own charge z_0 , represented by the intra-atomic repulsion U_0 . c_{01} corresponds to the shift for atom 0 due to neighboring charges z_1 's that are 2.35 Å apart from atom 0 in the same unit cell (interatomic repulsion $2e^2/2.35$) and due to charges z_1 's in the other unit cells (Madelung energy $-0.732W$). Other coefficients are derived similarly. Necessary tight-binding parameters for H including the intra-atomic repulsion energy are taken from Ref. 13 and others for Ge and Si are taken from Ref. 12. Once all the constants are determined, numerical solution is easy after a routine matrix inversion. A similar procedure applies to the π -chain case.

It should be noted that in the present formalism, we do not have any quantity corresponding to a chemical potential. We may tend to think that electrons will flow from an atom with a higher occupied level to an atom with a lower occupied level, and a certain quantity (chemical potential) becomes the same over the entire system in equilibrium. Diagonal elements ε_i 's do not play the role of this chemical potential. Indeed electrons do flow from a higher-occupied-level atom to a lower-occupied-level atom, but the flow stops before the diagonal elements become equal. This is clearly seen in Eqs. (1)–(3), where the difference in ε_i 's supports nonzero charges.

Once the charges are calculated, it is straightforward to obtain the band structures with a tight-binding method. The charges do not change the band shape, but shift the entire adatom bands upwards if adatoms are negatively charged, or downwards if positively charged. This shift occurs with the change of the Fermi energy, and hence semiconductor chains are unintentionally doped because of this charge transfer.

The bands for σ chains are given by

$$\varepsilon(k) = \{\varepsilon_a + \varepsilon_b \pm [(\varepsilon_a - \varepsilon_b)^2 + 8V_{sp\sigma}^2 \sin^2 kd]^2\}^{1/2} / 2, \quad (6)$$

where the lower and upper signs correspond to the valence and conduction bands, respectively. d is the adatom lattice spacing equal to 3.84 Å, and k is the momentum along the chain. $V_{ll'm}$ is an off-diagonal element between orbitals l and l' (either s or p) for m bonding (either σ or π), and are

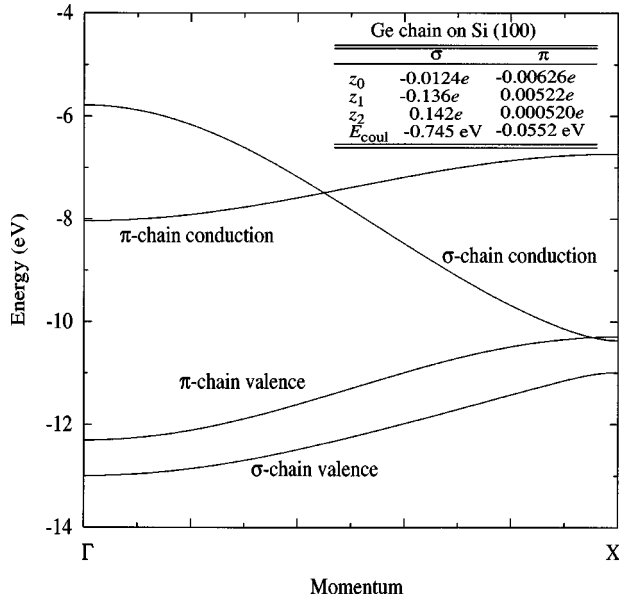


Fig. 5. Adatom band structures of σ and π chains with Ge adatoms on hydrogenated Si(100) surface and transferred charges (inserted table), where the vacuum level is the energy origin.

generally expressed with universal parameters in the form proportionate to d^{-2} .⁶ ε_a and ε_b are defined by

$$\begin{aligned}\varepsilon_a &= (\varepsilon_s + \varepsilon_p)/2 - (|V_{ss\sigma}| + |V_{pp\pi}|)\cos kd, \\ \varepsilon_b &= \varepsilon_p + 2|V_{pp\sigma}|\cos kd.\end{aligned}\quad (7)$$

In the above, ε_s and ε_p are *modified* diagonal matrix elements for s and p levels for adatom *after* self-consistent distribution of charges and the modification is calculated with Eqs. (4), while $V_{ll'm}$'s are unchanged. The valence and conduction bands for π chain are given, respectively, by

$$\begin{aligned}\varepsilon(k) &= (\varepsilon_s + \varepsilon_p)/2 - (|V_{ss\sigma}| + |V_{pp\pi}|)\cos kd, \\ \varepsilon(k) &= \varepsilon_p - 2|V_{pp\pi}|\cos kd.\end{aligned}\quad (8)$$

An inserted table in Fig. 5 summarizes the calculated charge amounts, z_0 , z_1 , and z_2 . They are quite small because of the electronic similarity between Ge and Si, and the linearization in deriving Eqs. (1)–(3) has been justified. Electrons are transferred from the Ge chain to the substrate atoms (thus unintentional p doping), and the shifts are -0.745 eV ($z_0 = -0.0124e$) and -0.0552 eV ($-0.00626e$) for σ and π chain, respectively, with e being the unit charge. The shift is larger in the σ chain than in the π chain. This is because the second nearest neighbors are H and Si, respectively, where a H atom can absorb electrons more effectively than a Si atom, due to the deeper H $1s$ level than the Si $3p$ levels. Since the C $2p$ levels are deeper than a Si $3p$ level, the opposite situation arises for C adatom chains. Electrons flow from the Si substrate atoms to the C adatoms, resulting in n doping. Because of such unintentional doping, electron filling is always a little off the exact full or half, and this makes the Peierls or Mott transitions¹⁴ irrelevant.

Figure 5 shows the band structures for σ and π chains. As is obvious in the plot, the σ chain has a typical band structure

made of symmetric and antisymmetric orbitals, sp and p orbitals, respectively, in a unit cell: the conduction band maximum and valence band minimum occur at Γ and the conduction band minimum and valence band maximum occur at the band edge X . This has been already apparent in Eq. (6). The π chain has two independent π bands made of two symmetric orbitals, sp and p . Since the p orbital is perpendicular to the chain as in Fig. 5, it is symmetric in the π chain, in contrast to the antisymmetric p orbital in the σ chain. Therefore, the band minimum occurs at Γ and the maximum at X for both valence and conduction bands. The entire structures for σ and π chains range around several eV, much wider than the bulk Si band gap. As discussed above this does not immediately mean poor isolation between the surface and bulk modes, and probably is not a serious problem, but needs to be studied in the future.

IV. SUMMARY

We consider the substrate effects on the adatom properties in the chemical bonding scheme. When the adatoms form chemical bonding to the substrate atoms, some electrons are exclusively used for covalent bonding, and only the remaining electrons can determine the adatom properties: the substrate kills some adatom electrons. Therefore, chain structures with group IV adatoms having two chemical bonds each to the substrate atoms, or group III adatoms having one chemical bond, are semiconductors, as well as group II adatoms with no chemical bond.

A main concern in this scheme is that the electron wave function may not be localized in an adatom structure, but penetrate deep into the substrate. This is in fact the case for an s - p uncrossing substrate such as alkali halide crystals. In turn, adatom states are localized at the surface if the substrate is s - p crossing such as many semiconducting and metallic crystals. On an s - p crossing substrate, we can eliminate unwanted surface states by saturation with H atoms, where elimination of dangling bonds means elimination of surface states (complementary situation for an uncrossing substrate). Ge adatom chains are studied using a self-consistent tight-binding method, and it is shown that two different kinds of chains are possible regardless of exactly the same lattice spacing, σ and π chains, depending on the geometrical relation between the covalent bonds and the chain direction, with unintentional doping. All of them are due to the substrate through the chemical bonds, and the electronic properties have to be assigned for the combination of the adatom and substrate systems in the chemical bonding scheme.

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