PRECISE NANOELECTRPONICS WITH ADATOM CHAINS

Toshishige Yamada*
MRJ, NASA Ames Research Center, M/S T27A-1, Moffett Field, California 94035-1000

ABSTRACT

Adatom chains on an atomically regulated substrate will be building components in future precise nanoelectronics. Adatoms need to be secured with chemical bonding, but then electronic isolation between the adatom and substrate systems is not guaranteed. A one-dimensional model shows that good isolation with existence of surface states is expected on an s-p crossing substrate such as Si, Ge, or GaAs, reflecting the *bulk* nature of the substrate. Isolation is better if adatoms are electronically similar to the substrate atoms, and can be manipulated by hydrogenation. Chain structures with group IV adatoms with two chemical bonds, or group III adatoms with one chemical bond, are semiconducting, reflecting the *surface* nature of the substrate. These structures are unintentionally doped due to the charge transfer across the chemical bonds. Physical properties of adatom chains have to be determined for the unified adatom-substrate system.

I. INTRODUCTION

When the gate length is reduced to 0.07 μm in a field-effect-transistor, the number of dopant atoms in the active region is no longer macroscopic, typically less than a hundred [1-3]. The spatial distribution of these dopant atoms fluctuates statistically from device to device even though each device is identically designed and fabricated, and this places a serious limitation on integration density. If device fabrication with atomic-scale accuracy [3] is required to overcome this problem, then it would be logical to create the entire electronics with components that are atomically precise, ordered, and preferably simple. This can be called precise nanoelectronics. Atomic chains, which are precise structures of adatoms created on an atomically regulated surface using atom manipulation technology [4], would become constituent components in future electronics. All the adatoms are placed at designated positions on a substrate, and all the device structures are precise, free from any statistical deviations. It was predicted using a tight-binding method with universal parameters [5, 6] that Si chains were metallic and Mg chains were semiconducting regardless of the lattice spacing [7], and a possible doping scheme was also proposed [8], when all the influences of the substrate were neglected for mathematical simplicity.

In practice, the substrate is quite influential on adatom chain properties, since the substrate must serve as a template for mounting the adatoms so that they are confined with a reasonable strength, and yet it must be electronically isolated from the adatom system. There are two possible physical mechanisms to secure adatoms at designated positions: Van der Waals bonding and chemical bonding. To evaluate the former strength, an *ab initio* study has been performed for a Mg adatom on the hydrogenated Si (111) surface [9] using a cluster model of $Si_{13}H_{22}$. It turns out that the Mg adatom will not be confined satisfactorily even at liquid-helium temperatures, with a Van der Waals potential as small as

0.39 meV [10]. The situation may not improve drastically for other kinds of substrates. Thus, we need to rely on the chemical bonding scheme. The main concern with this scheme is electronic isolation: the adatom wave function penetrates deep into the substrate through chemical bonds, and independent adatom structures couple, leading to unwanted cross talk. This problem is closely related to surface localization or how the wave function decays into the substrate. We use a chain model and clarify the existence conditions for surface states. H atoms can manipulate the surface states in a complementary manner on two distinct types of substrates. A method for obtaining semiconducting adatom chains is described with special requirements for the number of chemical bonds.

II. SURFACE LOCALIZATION AND ELECTRONIC ISOLATION

Edge (or end) states, zero-dimensional counterparts of higher-dimensional surface states, will be studied by using a chain model to represent a substrate. Surface states are supported by many atomic planes parallel to the surface as we will see later. Besides the difficulty in multi-dimensional modeling with many layers, the physics we are interested in is essentially one-dimensional, so the chain model suffices for a qualitative study. In fact, the wave function decays vertically since a reflection from each atomic plane interferes more destructively at a deeper point. This destructive interference is the origin of the surface states, and is one-dimensional in nature. In application of the edge state results to surface states, we can rely on a perturbation picture. When infinitely separated chains are brought together side by side in an array to form a finite substrate so that chain edges will form substrate surfaces, the energy levels corresponding to the edge states start widening. Since the bulk valence and conduction bands are widening, the bulk band gap is narrowing. As long as chains are distant, the adatom band widths are narrow and the entire adatom bands are located inside the bulk band gap. In this situation, the existence conditions for the edge states are equivalent to those for the surface states. When chains are brought closer, the adatom bands may overlap with the bulk bands, but the valence band maximum and conduction band minimum that are most important for electronics applications edge to remain inside the bulk band gap. Thus, the behavior of the edge states will survive in this limit. In the following, energy levels for a finite chain with edge adatoms are calculated as a function of lattice spacing d. Such plots show how surface states originate from atomic levels of constituent atoms as d is reduced and the crystal is formed [11, 12].

We might think intuitively that unsaturated (dangling-bond) states always localize at the surface, but this is not the case. Figure 1 shows electronic states of a Si atomic chain with an s-orbital and a p-orbital (representing symmetric and antisymmetric bases) as a function of atomic spacing d, calculated with the tight-binding theory with universal parameters [5, 6]: (a) energy levels and (b) edge population for states with thick line in unsaturated chain of 24 Si atoms; (c) and (d) are the same set of plots for a hydrogenated chain of 22 Si atoms. These results are essentially the same if the number of atoms is greater than 16. In both unsaturated and hydrogenated cases, the majority of levels, bulk-penetrating modes, behave similarly. When d is large, we see 3s and 3p bands in principle. Band widths increase as d is reduced. At $d \sim 2.7$ Å, both bands meet. This is an s-p crossing point and the spacing is denoted by d_{spc}. For $d < d_{\mathrm{spc}}$, a band gap reopens.

In the unsaturated case, edge states appear for $d < d_{\mathrm{spc}}$ as shown in Fig. 1(b). They are significant mixtures of s- and p-states and there is no apparent correlation for isolated atomic states. There are two edge states, one from the valence band and the other from the conduction band as is obvious by examining the number of states, and they constitute symmetric and antisymmetric modes for the chain center. Twenty-four states will be filled if all the atoms, including adatoms, are assumed to create two chemical bonds to the neighboring chains, and thus the edge states are half-filled. Since the filling can be changed by changing the number of adatom chemical bonds, we can eventually design metallic or semiconducting structures using this property as will be discussed in Sec. III.

In the hydrogenated case, edge states appear for $d > d_{spc}$. They are mostly s-like as in Fig. 1(d), and are identified as isolated 1s states in H. For $d < d_{spc}$, edge states disappear. Thus, the edge states in the hydrogenated case behave in a complementary manner to those in the unsaturated case. Counting an electron from each H atom, twenty-three states are filled, and edge states are again half-filled if the substrate atoms create two chemical bonds to the neighboring chains.

The physical mechanism for this complementary behavior can be intuitively understood as follows. Figure 2 schematically shows the envelope of a wave function ϕ at the vacuum boundary. For $d < d_{spc}$ in the unsaturated case, ϕ can connect smoothly into the vacuum and there exist edge states. A H atom provides a symmetric 1s-like wave function (no p-orbitals involved) in the cell, and flips $d\phi/dx$ without changing the value ϕ at the vacuum boundary. Therefore, once hydrogenated, ϕ cannot connect smoothly without having a notch, and edge states are eliminated. For $d > d_{spc}$ in the unsaturated case, ϕ has a notch and edge states are forbidden. When hydrogenated, the smooth connection is now possible because of the flip of $d\phi/dx$, and edge states appear.

When a crystal has a natural d such that $d < d_{spc}$, it is called s-p crossing, and when $d > d_{spc}$, s-p uncrossing. Examples of s-p crossing crystals are semiconductors such as Si, Ge, or GaAs and many metals, and those of s-p uncrossing crystals are alkali halides, such as LiF or KCl [11]. Practically, semiconductor substrates may be better since they are widely used in the current device technologies, can easily have an atomically regulated surface, and are s-p crossing, supporting surface states at dangling bonds.

Edge states are quite robust. In his original work [11], Shockley assumed geometrical symmetry for the chain center, but it turns out that this assumption is not essential for the existence of edge states as he had predicted. In order to see it, we have studied an unsaturated a chain asymmetric with respect to the central atom. Edge states still appear in the main band gap for $d < d_{spc}$, in the same way as they do in the symmetric cases. Different adatoms having both s- and p-orbitals (thus excluding H) can also create edge states for $d < d_{spc}$, but localization is better for electronically similar adatoms for $d < d_{spc}$. This is more important in a realistic three-dimensional case, where the band gaps are narrower.

We need to examine practical effects on the existence of the surface states. First, an adatom may not sit directly on a substrate atom in many situations, but the above localization results are insensitive to the detail of the position. Second, there are many different surfaces for a given crystal, but the results are again independent of the surface orientation. As long as the substrate is s-p crossing, the surface states exist on all the substrate surfaces: the substrate *bulk* properties determine the existence of the surface states. However, all the quantitative results such as the decay length of the wave function or the edge state energies do sensitively depend on the adatom positions, the adatom species, or the substrate surface orientation.

III. SEMICONDUCTING CHAINS WITH Ge ADATOMS ON Si (100)

Semiconducting adatom chains are obtained by either group IV adatoms with two chemical bonds each, or group III adatoms with one chemical bond each, to substrate atoms. A tight-binding view explains this in Fig. 3: (a) group IV and (b) group III adatoms, respectively. In Fig. 3(a), an adatom forms four sp^3-hybrid orbitals and is ready for chemical bonding to substrate atoms. When two sp^3-orbitals meet, they form bonding and antibonding orbitals separated by double the covalent energy [5], typically on the order of several eV. The remaining two dangling sp^3-orbitals will rehybridize and form an sp-orbital and a p-orbital [5, 13]. If these adatoms are arranged periodically, they form adatom bands. The sp-orbital forms a valence band and the p-orbital forms a conduction band. Since two additional electrons are provided from substrate atoms, we accommodate six electrons in total per unit cell. Thus, two bonding orbitals are filled and create two chemical (covalent) bonds, and the adatom valence band is fully filled, resulting in a semiconducting adatom structure.

In Fig. 3(b), the discussion runs parallel to the above. The difference is that in rehybridization, we now have two sp-orbitals and two p-orbitals, and one of two sp-orbitals is used for chemical bonding to a substrate atom. Two p-orbitals form two conduction bands corresponding to σ- and π-configurations, while the other sp-orbital forms a valence band. Including an electron from the substrate atom, we now have four electrons per unit cell and they fully occupy the adatom valence band as well as a bonding orbital (covalent bond), resulting again in a semiconductor.

Ge adatom structures on the Si (100) unreconstructed surface with two dangling bonds in an inset of Fig. 4 are a good example for a semiconducting chain achieving electronic isolation. Unused Si dangling bonds are hydrogenated to eliminate unwanted surface states. The ideal tetrahedral angles are assumed everywhere. There are two types of adatom chains with the same lattice spacing of 3.84 Å, σ- and π-chains, depending on the dangling sp^3-orbitals arrangement. No rehybridization is assumed for dangling bonds in the figure for clarity, but in fact resultant adatom bands are not influenced by whether dangling bonds are rehybridized or not, or mathematically the choice of the bases.

Taking into account the charge transfer effects among atoms up to the second nearest neighbors [13], we obtain adatom band structures in Fig. 4. The σ-chain has a conduction band minimum and a valence band maximum both at X, typical to one-dimensional s-p bands, while the π-chain has a conduction band minimum at Γ and a valence band maximum at X, because of two independent π-bands involved. The band widths are much wider than the Si bulk band gap (1.1 eV), and we expect that there would be a significant overlap between adatom and bulk Si bands. The situation is more serious in the π-chain since the adatom band gap is as wide as 4 eV, so that at least either the conduction band or the valence band will have an entire overlap with the bulk bands.

The overlap does not immediately mean poor isolation. Surface and bulk states may be able to exist independently. This is at least not contradictory to the experimental findings. In fact, a Si (111) substrate was studied using scanning tunneling microscopy, and a normalized-conductance plot as a function of voltage, known to correspond to the density of states, showed five peaks, four attributed to surface states and one to bulk states [16]. These peak positions were consistent with those of uncoupled, unperturbed surface and bulk states [14]. We may argue that the coupling between these states was so weak that no significant modulation in peak positions occurred, although the experiment did not directly detect electronic isolation in the context of device applications.

Adatoms are slightly depleted (z_0) in Fig. 4 by $-0.0124e$ and $-0.00626e$ (e the unit charge) and the entire adatom bands are shifted by -0.754 eV and -0.0552 eV in the σ- and π-chains, respectively. Both chains are positively charged, and the Fermi energy is slightly below the valence band maximum, resulting in unintentional p-doping. This simply reflects that the 4p levels in Ge are slightly shallower than the 3p levels in Si (the same relation for the sp^3-hybrid levels), so that electrons tend to flow from the Ge adatoms to the Si substrate atoms. In fact in the π-chain, the first and second nearest neighbors (both Si) are accumulated slightly. In the σ-chain, the first neighbors (Si) are depleted, while the second neighbors (H) are accumulated. This is because the 1s level in H is deeper than the relevant p-levels in Si or Ge so that H atoms tend to absorb electrons from neighbors more efficiently. Since the 2p levels in C are deeper than the 3p levels in Si, the electron flow is opposite, from the Si substrate atoms to the C adatoms. Thus, C adatom chains will be unintentionally n-doped. When the conditions for a semiconductor are not satisfied, adatom structures are expected to be metallic, as long as the Peierls transition or Mott transition [15] are irrelevant. For different adatoms, these transitions are not likely to occur since adatom structures are unintentionally doped through charge transfer as discussed above, and the electron filling is always different from exact one-half, one-third, etc.

The tight-binding view developed here is insensitive to the details of the adatom positions. The crucial information is how many adatoms and dangling bonds there are per unit cell. As long as these numbers do not change, the electron filling remains the same in the adatom bands and the same criteria apply to judge whether a given adatom chain is semiconducting or not. Since different substrate surfaces have generally a different number of dangling bonds per unit cell, the *surface* changes the electronic properties of adatom chains, in sharp contrast to the above existence conditions. The details of the adatom bands as well as other quantitative results do depend on the exact adatom positions.

IV. SUMMARY

For the developement of precise nanoelectronics, electronic isolation between the adatom and substrate systems is shown to be achieved through the creation of localized adatom surface states with chemical bonds. The surface states exist at the dangling bonds on an s-p crossing substrate such as Si, Ge, or GaAs. The isolation is better if the adatoms are electronically similar to the substrate atoms. We can eliminate such surface states by hydrogenation on s-p crossing substrates. Group IV adatoms with two chemical bonds each, or group III adatoms with one chemical bond each, can form semiconducting structures. As an example for a semiconducting adatom chain with electronic isolation, σ- and π- Ge adatom chains on Si (100) were studied, and unintentional p-doping was pointed out. In the chemical bonding scheme, we cannot define intrinsic properties of an adatom chain. The existence of the surface modes depends on the bulk properties of the substrate, and the electron filling of the adatom bands depends on the surface properties of the substrate. Adatom properties have to be considered within a unified adatom-substrate system.

ACKNOWLEDGEMENT

The author gratefully acknowledges Dr. M. Meyyappan for fruitful discussions and continuous encouragement during the course of this work. He is grateful to Dr. C. W. Bauschlicher, Jr., Dr. H. Partridge, and Dr. B. A. Biegel for many helpful discussions, and to Dr. T. R. Govindan for advice and encouragement.

REFERENCES

[*] Electronic address: yamada@nas.nasa.gov

[1] H.-S. Wong and Y. Taur, Tech. Dig., Int. Electron Devices Meeting, 705 (1993).
[2] J. -R. Zhou and D. K. Ferry, IEEE Comp. Sci. Engr. **2**, 30 (1995).
[3] J. R. Tucker and T.-C. Shen, Solid-State Electronics **42**, 1061 (1998).
[4] For example: D. M. Eigler and E. K. Schweizer, Nature (London) **344**, 524 (1990); I.-W Lyo and Ph. Avouris, Science **253**, 173 (1991); H. J. Hamin, S. Chiang, H. Birk, P. H. Guenther, and D. Ruger, J. Vac. Sci. Technol. B **9**, 1398 (1991); M. F. Crommie, C. P. Lutz, and D. M. Eigler, Science **262**, 218 (1993); Ph. Ebert, M. G. Lagally, and K. Urban, Phys. Rev. Lett. **70**, 1473 (1993); Ph. Avouris, I.-W. Lyo, and Y. Hasegawa, J. Vac. Sci. Technol. A **11**, 1725 (1993); H. Uchida, D. Huang, F. Grey, and M. Aono, Phys. Rev. Lett. **70**, 1437 (1993); C. T. Salling and M. G. Lagally, Surf. Sci. **265**, 502 (1994); A. Yazdani, D. M. Eigler, and N. D. Lang, Science **272**, 1921 (1996).
[5] W. A. Harrison, *Electronic Structure and Properties of Solids* (Freeman, San Francisco, 1980).
[6] W. A. Harrison, Surf. Sci. **299/300**, 298 (1994); W. A. Harrison, Phys. Rev. B **24**, 5835 (1981).
[7] T. Yamada, J. Vac. Sci. Technol. B **15**, 1019 (1997); T. Yamada, Y. Yamamoto, and W. A. Harrison, J. Vac. Sci. Technol. B **14**, 1243 (1996).
[8] T. Yamada, J. Vac. Sci. Technol. A. **16**, 1403 (1998).
[9] J. W. Lyding, T.-C. Shen, J. S. Hubacek, J. R. Tucker, and G. C. Albeln, Appl. Phys. Lett., **64**, 2010 (1994); T.-C. Shen, C. Wang, G. C. Abeln, J. R. Tucker, J. W. Lyding, Ph. Avouris, and R. E. Walkup, Science, **268**, 1590 (1995).
[10] T. Yamada, C. W. Bauschlicher, Jr., and H. Partridge, to be published in Phys. Rev. B **59**, 1999.
[11] W. Shockley, Phys. Rev. **56**, 317 (1939).
[12] W. Shockley, *Electrons and Holes in Semiconductors* (Van Nostrand, Princeton, 1950).
[13] W. A. Harrison and J. E. Klepeis, Phys. Rev. B **37**, 864 (1988); J. E. Klepeis and W. A. Harrison, J. Vac. Sci. Technol. B **6**, 1315 (1988); J. E. Klepeis and W. A. Harrison, Phys. Rev. B **40**, 5810 (1989).
[14] J. A. Stroscio, R. M. Feenstra, and A. P. Fein, Phys. Rev. Lett. **57**, 2579 (1987).
[15] R. Peierls, *Quantum Theory of Solids*, (Oxford, Oxford, 1955); N. F. Mott and E. A. Davis, *Electronic Processes in Non-crystalline Materials*, (Clarendon, Oxford, 1979).
[16] D. Allen and E. J. Mele, Phys. Rev. B **31**, 5565 (1985).

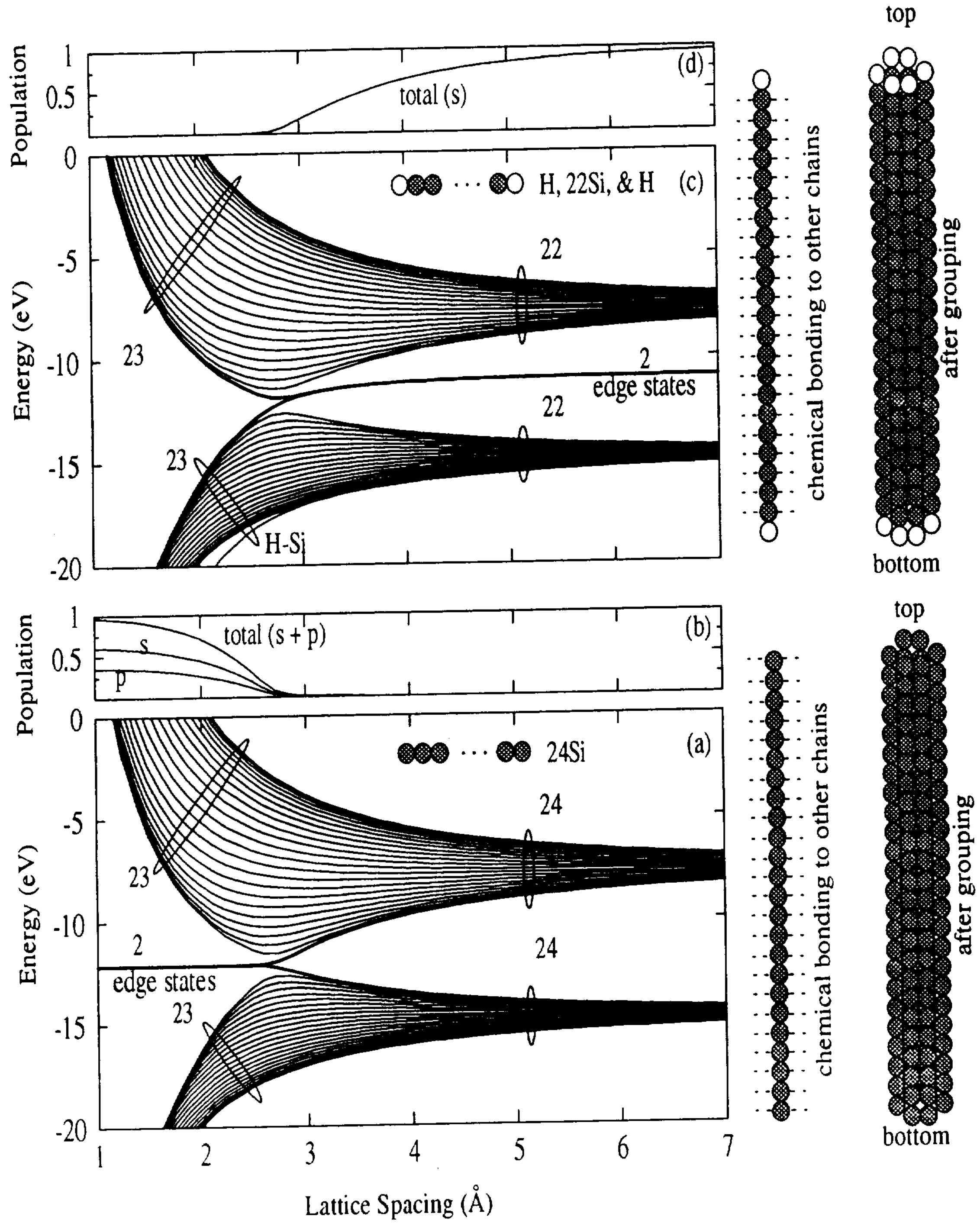


FIG. 1. Electronic states as a function of lattice spacing: (a) energy levels and (b) edge population for states with thick line in 24 Si chain; (c) and (d) the same plots in 22 Si chain with two edge H adatoms.

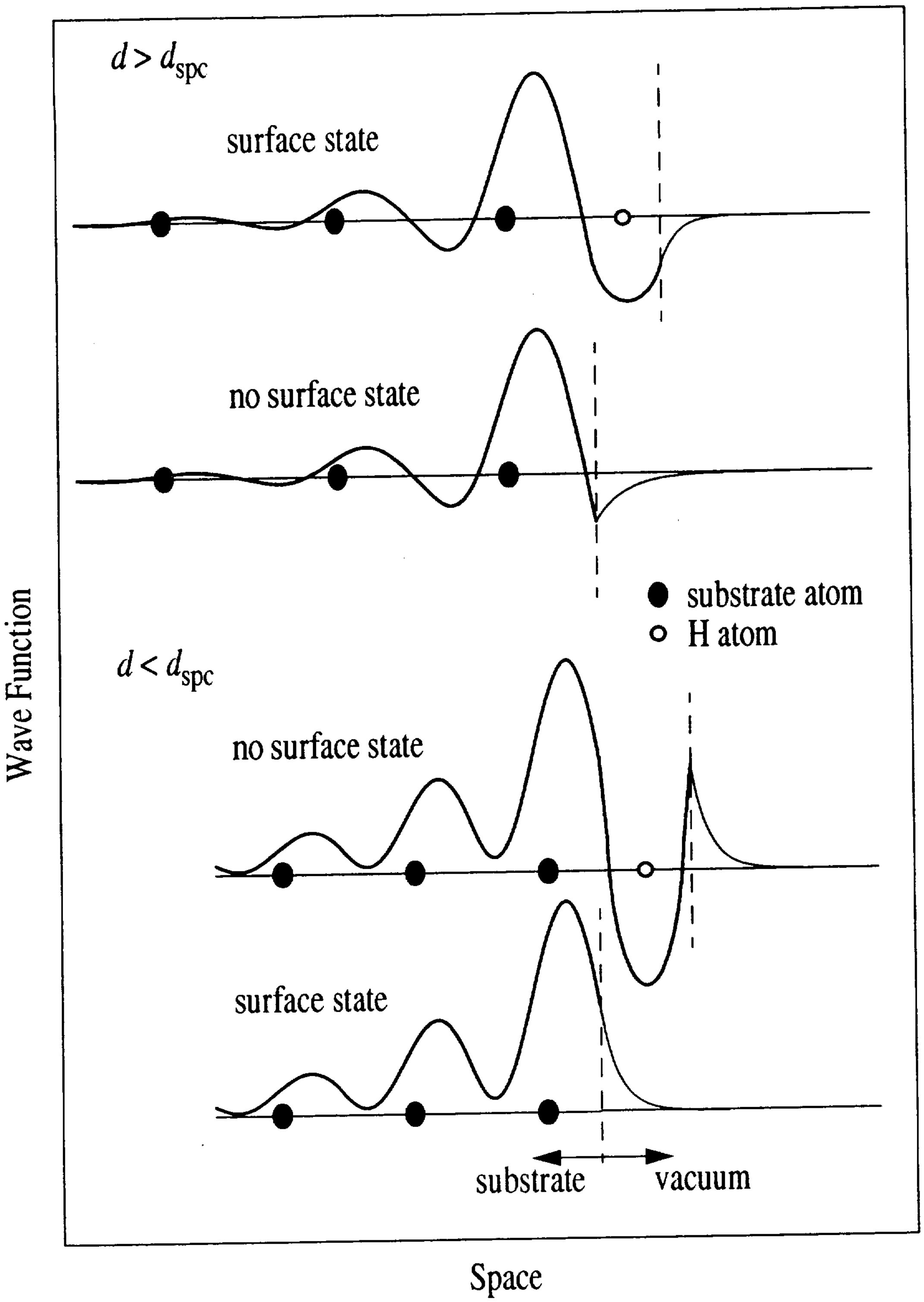
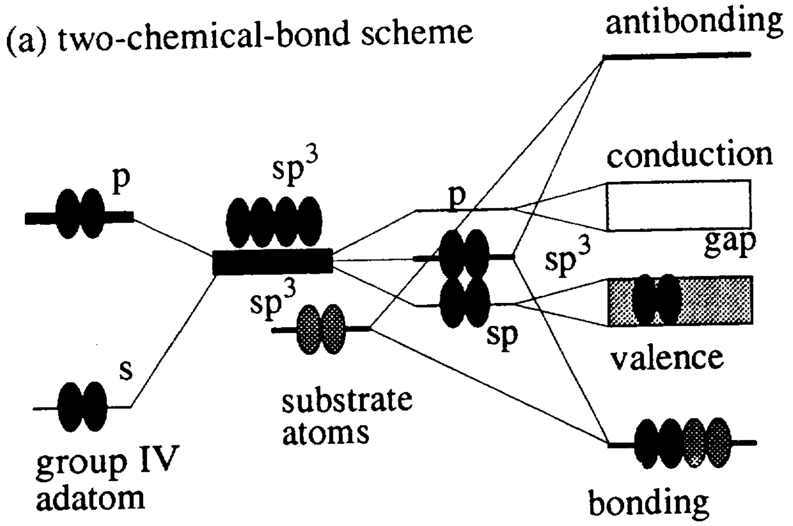
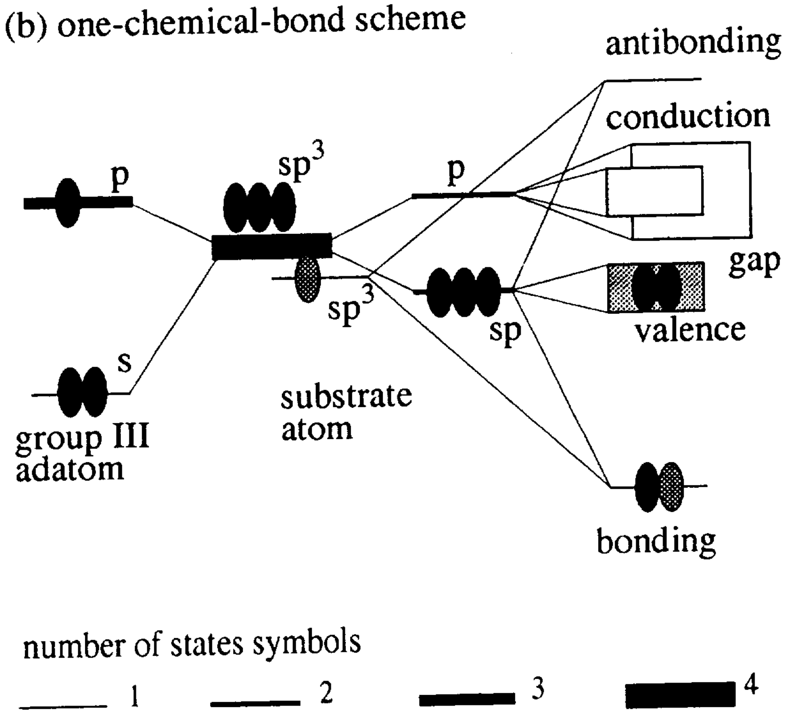


FIG. 2. Schematic plots of wave functions for unsaturated and hydrogenated cases at the vacuum boundary for $d < d_{\text{spc}}$ (lower two) and $d > d_{\text{spc}}$ (upper two).

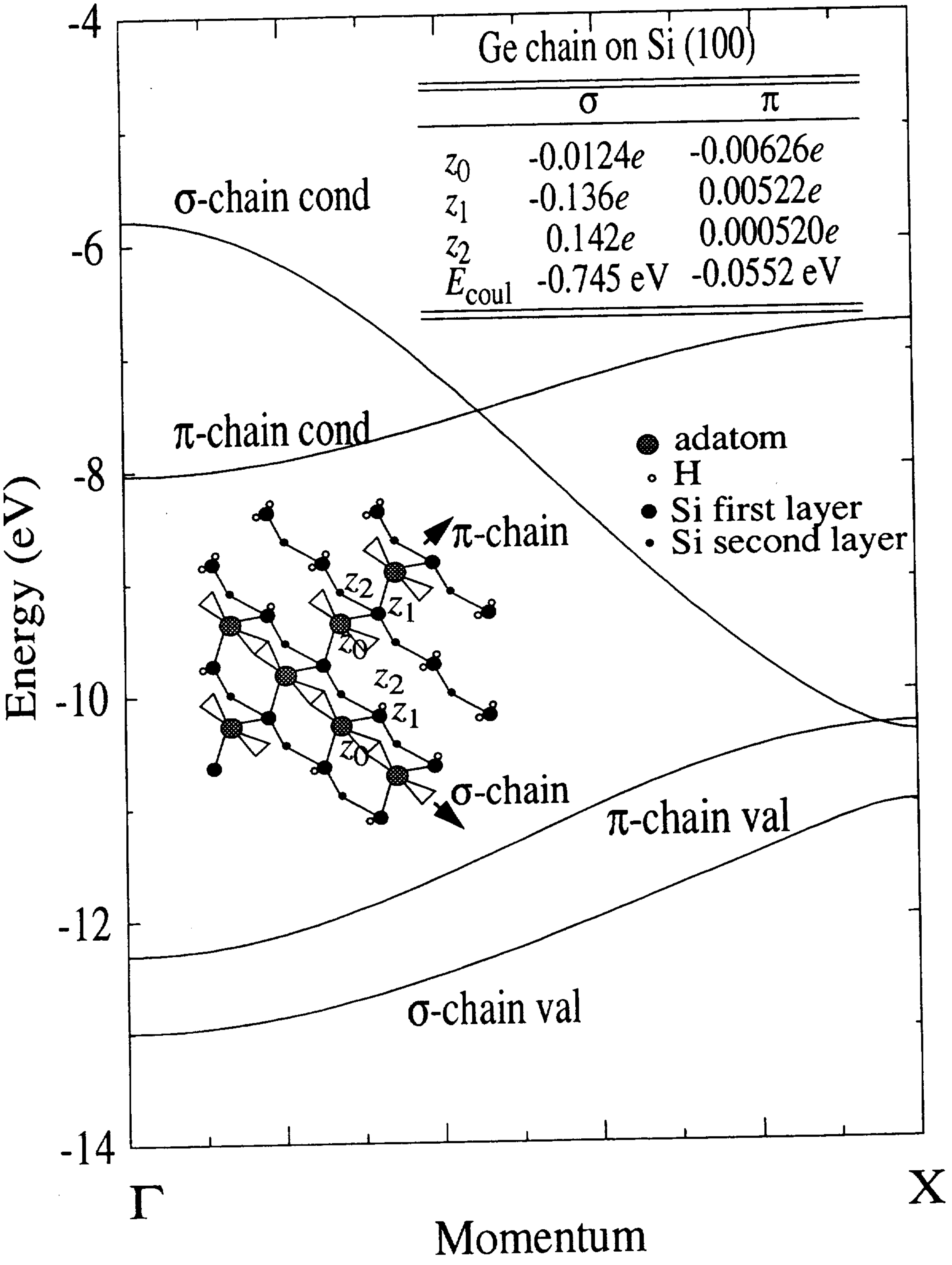


(a) two-chemical-bond scheme



(b) one-chemical-bond scheme

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.



Ge chain on Si (100)

	σ	π
z_0	-0.0124e	-0.00626e
z_1	-0.136e	0.00522e
z_2	0.142e	0.000520e
E_{coul}	-0.745 eV	-0.0552 eV

FIG. 4. Band structures for σ- and π-chains with Ge adatoms on hydrogenated Si(100) surface and transferred charges.