Doping scheme of semiconducting atomic chains

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Atomic chains, precise structures of atomic scale created on an atomically regulated substrate surface, are candidates for future electronics. A doping scheme for intrinsic semiconducting Mg chains is considered. In order to suppress the unwanted Anderson localization and minimize the deformation of the original band shape, atomic modulation doping is considered, which is to place dopant atoms beside the chain periodically. Group I atoms are donors, and group VI or VII atoms are acceptors. As long as the lattice constant is long so that the s-p band crossing has not occurred, whether dopant atoms behave as donors or acceptors is closely related to the energy level alignment of isolated atomic levels. Band structures are calculated for Br (p-type) and Cs-doped (n type) Mg chains using the tight-binding theory with universal parameters, and it is shown that the band deformation is minimized and only the Fermi energy position is modified. [S0734-2101(98)59003-3]

I. INTRODUCTION

When the transistor size is reduced beyond 0.1 μm, there arise a lot of unwanted effects which will lead to malfunctioning of the devices. It has been pointed out[1] that the spatial fluctuation of dopant atoms would be a serious problem in the 0.07 μm gate length regime. The number of dopant atoms in the channel in such a small device is typically less than 10^2 and electrons see discrete dopant atoms that are scattered randomly inside the channel. This causes significant deviation in input/output characteristics from device to device even though devices are designed to be the same, thus placing limitation for integration. Controlling dopant positions within atomic scale accuracy is practically impossible.

A fundamental solution to the above problem is to create electronics with simple but atomically precise structures using rapidly advancing atom manipulation technology.[2] Atomic chain electronics[3] falls into this category. Foreign atoms are placed as adatoms on an insulating substrate surface. The surface is atomically flat, regulated by surface reconstruction, for example, and provides a two-dimensional periodic potential to hold adatoms. We manipulate the lattice constant d in these adatom structures, usually in the range longer than the natural one, and design the electronic properties. Such long d is necessary to eliminate the possible spontaneous deformation such as dimerization, but the electron wave still can spread over an entire structure coherently, as demonstrated in Ref. 4 where a Bloch wave was observed along a dangling bond chain.

It has been shown theoretically[3] that Si chains are metallic and Mg chains are semiconducting, regardless of d. In order to create electronics, it is mandatory to establish a doping method for semiconducting Mg chains, but it is not straightforward. The random replacement of Mg atoms with dopant atoms will result in unwanted Anderson localization,[5] which localizes electrons in solids and is most marked in a one-dimensional system. However, periodic replacement will cause a serious deformation in the band structure, and may result eventually in a different material with little relation to the original. In order to overcome this dilemma, atomic modulation doping is considered, which is to place dopant atoms beside the chain periodically.

The energy level ordering of Mg and the dopant atom has a close relation for long d where the s-p band crossing[3,6–8] has not occurred. This is in sharp contrast to the usual doping for macroscopic Si, where the number of chemical bonds decides whether the dopant is an acceptor or a donor.[6] It is shown that group I atoms serve as donors and group VI and VII atoms serve as acceptors. In the following, the doping scheme is discussed in detail, with examples of band structures for Mg chains calculated using the tight-binding theory with universal parameters.[8,9]

II. s-p BAND CROSSING AND METALLIC/SEMICONDUCTING ELEMENTS

As long as a system has periodicity and a one-electron picture prevails, the behavior of the electronic states as the lattice constant d is reduced from infinity can be classified to some prototype patterns depending on the symmetry and dimension.[3,6–8] When d is large, the energy levels are in principle those of isolated atoms, e.g., an s-like state and three p-like states per atom, in addition to the stable core states. As d is reduced, the band widths become wider and wider, and at some stage they are so wide that one of the upper bands and the lower band touch. This is called s-p band crossing. With further reduction in d several scenarios are possible: (1) in diamond-structure crystals, these two bands stick together and a new band gap appears changing the partition of states, two lower states and two upper states, due to the sp^3 hybridization;[6–8] (2) in one-dimensional chains, the two bands repel each other to reopen a gap, without changing the number of upper and lower states;[3] (3) in two-dimensional square arrays, the two bands overlap significantly, and there appears a large unified allowed energy region.[3]

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Using the tight-binding theory with universal parameters,[8,9] it has been shown[3] that Si chains are always metallic with the band crossing at $d = 2.7$ Å, while Mg chains are always semiconducting with the band crossing at $d = 4.2$ Å. This can be understood based on the fact that the highest occupied molecular orbital (HOMO) in a Si atom is $3p$ and is partially filled while the HOMO in a Mg atom is $3s$ and fully filled, and the band structure of the chain follows scenario (2) as d is reduced.

III. ATOMIC MODULATION DOPING OF Mg CHAINS

Having found metallic and semiconducting elements, it is important to establish a scheme to form p- or n-type semiconductors. The typical doping concentration for modern Si devices is so small (at most $\sim 10^{20}$ cm^3, only ~0.1% are dopants) that the original Si band structure does not undergo major modifications. The doping changes the Fermi energy position and keeps the band shape the same, except for minor effects such as band gap narrowing.[10]

In atomic chain electronics, the ratio of dopant atoms to the host chain atoms may not be extremely small since a chain will be formed with preferably less than 10^2 atoms. Adoption of only one dopant atom per chain will destroy translational symmetry in the system and create a large potential barrier, which is not appropriate. Placing multiple dopant atoms randomly will cause the onset of unwanted Anderson localization.[5] The electrons spatially localize in the random potential created by dopant atoms and the resistance exponentially depends on the chain length under the coherent limit. Even if not all conditions for the Anderson localization are satisfied, there would still be a significant degradation in transport due to the random doping. This point has been elucidated experimentally[11] using a two-dimensional electron gas, where two doped samples were compared, one with spatially correlated dopant configuration and the other with random configuration, and a clear mobility enhancement for the former was observed. Therefore, we must dope periodically. However, if we simply replace chain atoms with dopant atoms periodically, dopant bands will appear and change the original band structure qualitatively. In order to overcome this dilemma, atomic modulation doping is considered. Dopant atoms are placed laterally, beside the Mg chain atoms at every N period. Because dopant atoms do not directly constitute the chain, the band deformation is minimized and the structure is still periodic.

This ideal is demonstrated using the tight-binding theory with universal parameters.[8,9] Figure 1(a) shows the band structure of an intrinsic Mg chain with the lattice constant $d_x = 5$ Å (x along the chain). a unit cell is assumed to contain three Mg atoms, so that $X = \pi/(3d_x)$, and thus original Mg bands are folded three times without any band gaps at the zone edges. The lower σ bands originated from $3s$ and $3p_x$ orbits are completely filled. The upper bands, separated with the only band gap, are completely empty and consist of a σ band originated from $3s$ and $3p_x$, and a degenerate π band originated from $3p_y$ and $3p_z$ normal to the chain. Figure 1(b) shows the band structure under atomic modulation doping,

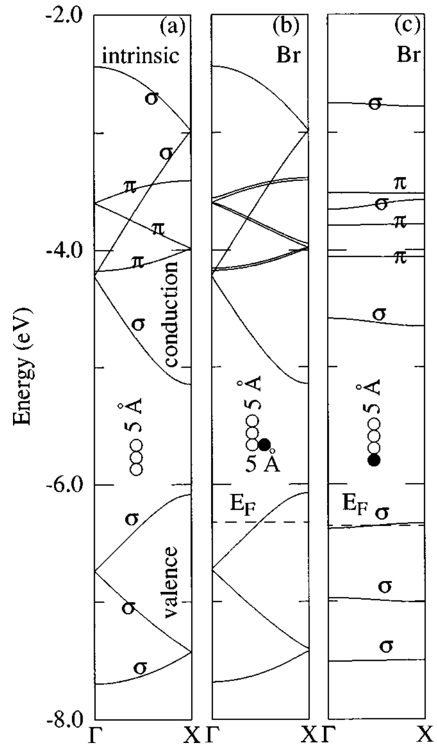

FIG. 1. Band structures of Mg chains with lattice constant $d_x = 5$ Å for different doping schemes: (a) instrinsic chain, (b) Br-modulation doped p-type chain with chain-dopant separation $d_y = 5$ Å, and (c) Br-directly doped p-type chain.

where an acceptor atom Br is placed at one side of every third Mg atom, 5 Å apart laterally, normal (y direction) to chain. All Br related bands are so deep, $3s$ (−27.0 eV) and $3p$ (−12.4 eV), that they cannot even be seen in the plot. Each Br atom accepts approximately one electron (less than one practically due to the Coulomb interaction as discussed later) to form fully filled $3p$ bands. the degeneracy in the π band is slightly lifted, but the band deformation is minimized and only the Fermi energy position (broken line) is modified. The period $N = 3$ introduces small band gaps opening at the zone edges, on the order of ~10 meV. Because of these band gaps, the valence band is divided into three, and the uppermost valence band is exactly half-filled. The system will not always be vulnerable to the Peierls or Mott transitions,[12] known as insulator transitions. In fact, if we increase the period N or the chain-dopant separation d_y, it is eventually possible to eliminate the small band gaps and make these effects irrelevant. We have satisfied the requirements of doping, to modulate the Fermi energy position without changing the band shape. Figure 1(c) shows the band structure of direct doping, where every fourth Mg atom is replaced by a Br atom, preserving the same doping density as (b). The degeneracy in the π band is not lifted because of the symmetry in the y and z directions, but wide band gaps open at the zone edges and there is very little correlation to the original in (a), resulting in a different material. Although the Anderson localization is avoided, all bands have a significantly flatter

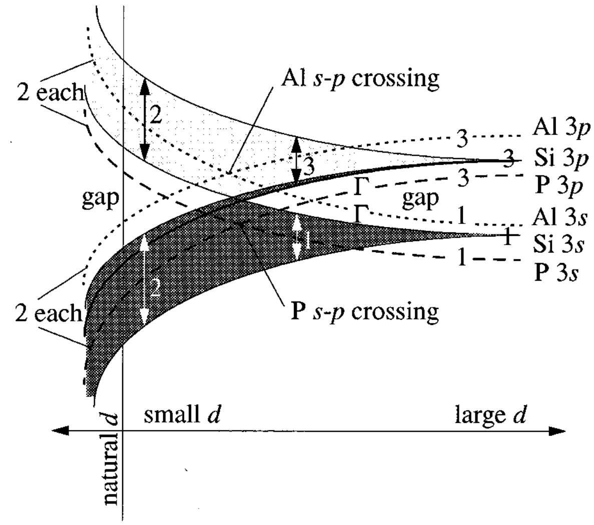

FIG. 2. Dopant levels in diamond-structure Si as a function of lattice constant d. Dotted lines indicate Al levels and broken lines P levels. Shades correspond to allowed energy regions, where electrons are filled in the darker shades. The number of states is indicated per atom of interest.

dispersion compared to (a), and this is certainly not beneficial for transport.[13]

One may wonder how to find acceptors and donors, and how the dopant levels in a chain or a crystal are correlated to the isolated atomic levels. For this problem, the diamond-structure Si crystal serves as an instructive example. It is known that group III atoms such as Al become acceptors, while group V atoms such as P become donors when substitutionally doped.[6] This is understood by a usual argument of counting the number of chemical bonds: an Al atom has one less chemical bond than a Si atom and thus behaves as an acceptor while a P atom has one more chemical bond and thus behaves as a donor. The energy levels align as the Si conduction band, the P donor level, the Al acceptor level, and the Si valence band in the descending order.[6] Both donor and acceptor levels are located inside the band gap. However, the HOMO levels of isolated Al and P atoms align as Al 3p (−5.71 eV), Si 3p (−7.59 eV), P 3p (−9.54 eV), and Si 3s (−14.79 eV)[9] in the descending order. Not only Al and P levels are reversed in the Si crystal, but Al 3p is not even located between Si 3s and Si 3p levels. This intriguing behavior is explained with the s-p band crossing. Figure 2 schematically shows how the atomic Si levels (solid lines) are modified to form bands, together with dopant levels (dotted lines for Al and broken lines for P), when the lattice constant d is reduced from infinity (scaling in all directions). Shades correspond to allowed energy regions, where electrons are filled within the darker shades. The number of states is indicated *per atom of interest,* and the partition weight for Si bands and dopant levels is not considered. Because of the usual thin, random doping, the dopant states are discrete and only null momentum (Γ) is allowed. s lines at Γ tend not to cross one another and p lines at Γ tend not to cross one another, either, and therefore, an s-p band crossing occurs for Al and P levels, respectively. Originally, the upper and lower dopant levels have three and one states, respectively, but after the crossing, the states are sp^3 hybridized and there are two states for each. Once the crossing occurs, the memory for the energy level ordering in isolated atoms is totally lost.

We have emphasized using a long lattice constant in atomic chain electronics for the mechanical stability, and fortunately this now makes the dopant selection much simpler for the reason above. We need to choose a donor atom with its HOMO shallower than the conduction band minimum, and an acceptor atom with its HOMO deeper than the valence band maximum. Judging from this criterion, group I atoms are donors, and group VI and VII atoms are acceptors, somehow reminiscent of the dopant selection for polymers.[14] The band deformation has to be minimized. Thus, Cs will be the best donor, since its 3s HOMO level of −3.37 eV is the shallowest in group I (except for unfamiliar Fr). This HOMO level is within the conduction band of a Mg chain with a typical lattice constant, e.g., 5 Å, causing some disturbance for the π bands but practically no serious effects overall. There are much wider choices for acceptors, since HOMO levels in group VI and VII atoms are quite deep, far below −10 eV. F may be the most preferable with the deepest HOMO in group VII, but Cl, Br, or S will also be fine. It should be emphasized that the usual argument of counting the number of chemical bonds does not work, (e.g., group I atoms are not acceptors and group III atoms are not donors), and the dopant levels are not within the band gap, either.

The reason for this unfamiliar dopant level position is entirely due to the choice of large lattice constant, and has nothing to do with the one dimensionality. Figure 3 shows the dopant positions of K-doped Mg chains: a dense chain with d_x=3 Å, (a) intrinsic (reference) and (b) K doped with d_y=3 Å; a sparse chain with d_x=5 Å, (c) intrinsic and (d) K doped with d_y=5.5 Å, so that we scale the structure in all directions. 3 Å is smaller than the Mg chain crossing point of 4.2 Å,[3] but would also be smaller than the natural Mg–K distance, so that the plots should be considered a gedanken experiment. In a dense chain with d_x=3 Å, an additional fairly flat band appears around −5.2 to −5.3 eV inside the band gap, and is identified as a dopant level (arrow). In a sparse chain with d_x=5.5 Å, the dopant level appears around −4.2 eV, and is, this time, within the conduction band. The dopant level is within the conduction band in the sparse chain but can move into the band gap in the dense chain if we go beyond the s-p band crossing.

It is recommended that the dopant atoms be placed far apart from the chain (increase the chain-dopant separation d_y) to minimize the band deformation. Figure 4 compares the band structure of Br-doped Mg chains with the same d_x=5 Å but different d_y: (a) 4, (b) 5, and (c) 6 Å, respectively. The deformation can be seen in the band gaps at the zone edges, and clearly decreases for wider d_y. We can use the probabilistic interpretation of wave functions and estimate the effective charge. Within the current calculation scheme using the free-atom term values (neglecting Coulomb interaction), the results are (a) Br: −0.960, Mg(I): 0.330, Mg(II): 0.315, (b)

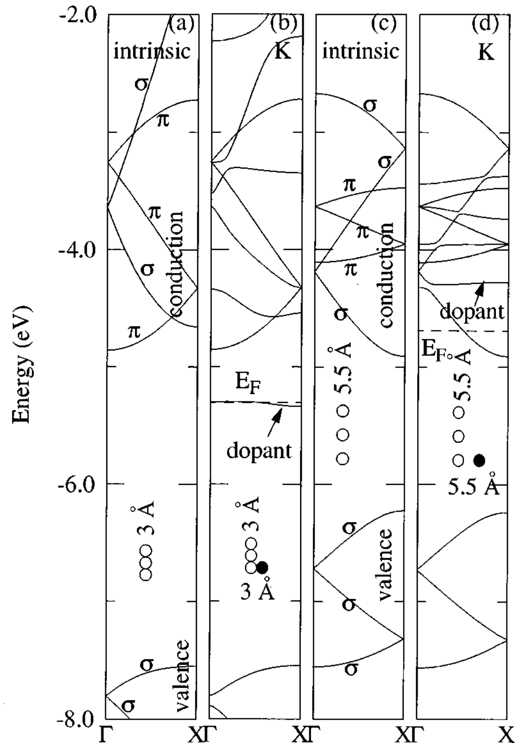

FIG. 3. Dopant level positions in Mg chains: small structures with lattice constant d_x=3 Å, (a) intrinsic and (b) K-doped with chain dopant separation d_y=3 Å; large structures with d_x=5.5 Å, (c) intrinsic and (d) K-doped with d_y=5.5 Å.

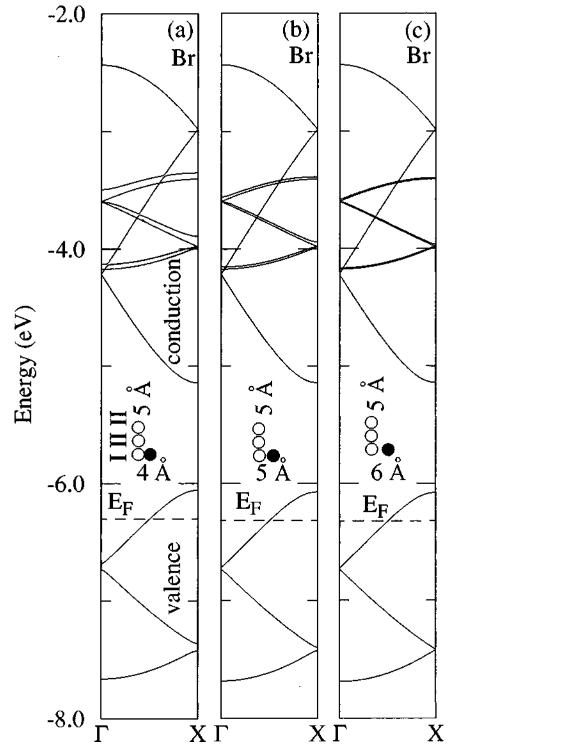

FIG. 4. Band structures of Br-doped Mg chains with the same lattice consatnt d_x=5 Å but different chain-dopant separations d_y: (a) 4, (b) 5, and (c) 6 Å.

Br: −0.984, Mg(I): 0.332, Mg(II): 0.326, and (c) Br: −0.993, Mg(I): 0.333, Mg(II): 0.330, where Mg(I) is the atom beside the Br atom and Mg(II)s are the remaining two atoms in a unit cell, and the charges are normalized to the unit charge. The total charge is conserved within a unit cell. We can observe a clear tendency for the dopant atom to be more charged for wider d_y, which may seem puzzling at first glance. However, a similar phenomenon is well known in a diatomic molecule, which can be analyzed using the tight-binding theory.[8] If two atoms $|\alpha\rangle$ and $|\beta\rangle$ have an isolated energy level E_α and E_β ($2V_3=E_\beta-E_\alpha>0$), respectively, and interact with $\langle\alpha|H|\beta\rangle=\langle\beta|H|\alpha\rangle=V_2$, then the probabilities to find an electron on atoms α and β are expressed by $(1+\alpha_p)/2$ and $(1-\alpha_p)/2$, respectively, where $\alpha_p=V_3/(V_2^2+V_3^2)^{1/2}$. Widening d_y corresponds to decreasing V_2 while fixing V_3, and this makes α_p approach unity, and the atoms are more charged. Wider d_y decreases the band deformation and would be preferred, although too wide d_y beyond some threshold would practically result in inefficient charge transfer. The uppermost valence band is always half-filled regardless of d_y.

We may need to consider the influences of Coulomb interaction. The charge transfer from Mg atoms to Br atoms would change the atomic levels of Br and Mg effectively (intra-atomic repulsion), which is modified by the Madelung interaction (interatomic attraction).[9,12] The substrate supporting the atomic chain will cause relaxation,[9] and this form of Coulomb interaction will be discussed in Sec. IV, but not here. The Coulomb charging energy is 9.78 eV for Br and 7.28/3=2.43 eV for Mg,[9] while the typical Madelung energy, e.g., for d_x=5 Å, is −2.34, −0.650, and −0.137 eV for Br, Mg(I), and Mg(II) assuming that the charges are −1, 1/3, and 1/3, respectively. Since the Madelung energy is not large enough to cancel the charging energy for this long d_x, the use of free-atom term values throughout the calculation is not quite appropriate: the problem will have to be solved self-consistently. This has not been done, but the qualitative results would remain the same due to the extremely shallow or deep HOMO levels in donor or acceptor atoms, respectively.

So far, we have assumed three Mg atoms and a dopant atom per unit cell. We can increase the period N and this reduces the band deformation, simply because the dopant atoms are more distant. For period N doping with group I atoms, the σ- and π-conduction bands are folded into N, respectively, with small band gaps opening at the zone edges. The lowest conduction band is σ and is half-filled. For group VII atom doping, the σ-valence band is folded into N and the upper-most valence band is half-filled. For group VI atom doping, the uppermost valence band is completely empty and the rests are completely filled. By adopting large N, we can also avoid the unwanted insulator transitions, due to the Peirels transition for group I and VII and due to the formation of band gaps for group VI.

Figures 5(a) and 5(b) compare the band deformation of Br-doped p-type Mg chains with the same $d_x=d_y$=5 Å but a different period N=3 and 6, respectively. The Brillouin zone in (b) is half of (a) and the number of dispersion curves

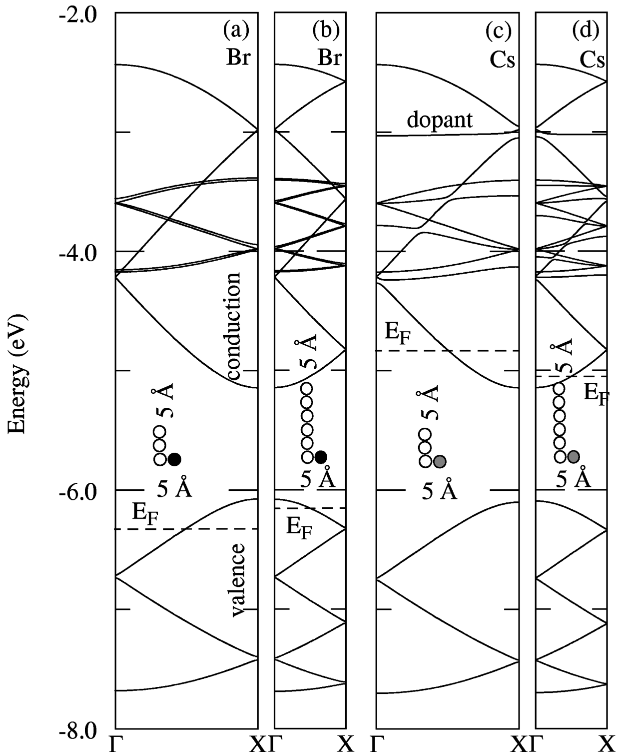

FIG. 5. Band structures of Mg chains with the same lattice constant d_x=5 Å and chain-dopant separation d_y=5 Å but different doping periods N: Br doped, (a) 3 and (b) 6; Cs doped, (c) 3 and (d) 6.

is double. The band gaps at the zone edges clearly reduce in (b). For example, the band gap at Γ around −6.7 eV is 23.6 meV in (a) and 12.9 meV in (b). Adopting further larger N will eventually eliminate these small gaps, and the nature of the half-filled band is less and less important. Figures 5(c) and 5(d) are the same plots for Cs doped n-type cases, and again the larger N reduces the band deformation. The atomic HOMO level of Cs is −3.37 eV[9] and the corresponding dopant level is located around −3 eV.[15] The dopant level is inside the conduction band and this causes large deformation for the π band but may not be harmful for device applications since it does not introduce any new forbidden regions in the conduction band.

IV. SUMMARY AND DISCUSSIONS

It is shown that intrinsic semiconducting Mg chains can be doped with an atomic-modulation-doping scheme, which is to place dopant atoms beside the chain periodically. This scheme controls the Fermi energy position with negligible band deformation, achieving the purpose of doping. As long as the lattice constant is long so that the s-p band crossing has not occurred, group I atoms are donors with their HOMO much shallower than the conduction band minimum, and group VI and VII atoms are acceptors with their HOMO much deeper than the valence band maximum. This is demonstrated with the tight-binding calculation with universal parameters using free-atom term values. Actual charge transfer between chain and dopant atoms will be modified with the Coulomb interaction but is would not change the qualitative results here.

Since chain and dopant atoms, adatoms, are charged in the current doping scheme, one may think that there would be Coulomb forces among adatoms, and they might be displaced from their ideal positions. We may be able to avoid this in a realistic situation where adatoms are placed on a substrate. A charged adatom on top of the substrate will create an electric field and polarizes the surrounding substrate atoms. This polarization in turn attracts the adatom towards the substrate. We can view this process as a formation of an image charge and a resulting image force. In fact, the image-charge concept prevails even in atomic dimensions,[9] and has been applied to several surface problems successfully with a macroscopic dielectric constant.[16] We demand that the image force be more dominant than other Coulomb forces to keep the ideal positions. This condition will be satisfied when the image charge is placed more closely to the original than any others (hence again prefer a chain of a long lattice constant) and the ratio of the image charge to the original $(\epsilon_{\rm sub}-1)/(\epsilon_{\rm sub}+1)$ is large, close to unity (thus prefer a large dielectric constant $\epsilon_{\rm sub}$). A H-terminated Si reconstructed surface[3] is a possibility, where all dangling bonds are saturated with H atoms and the adatoms do not form chemical bonding with the substrate atoms. Neutral adatoms will stay at the minima of a two-dimensional van der Waals potential. Charged adatoms will also be confined at the minima but with the help of an image potential, estimated to be several eV in this atomic dimension, owing to large $\epsilon_{\rm sub}$ (11.7) in Si. The image charge formation will eventually double the Madelung energy compared to the estimation in III, and cancel the intra-atomic Coulomb energy more effectively. One may concern whether the strong potential to hold adatoms will change the predicted chain properties, even qualitatively. This will not happen as long as chemical bonding is not formed, since the potential (the intra- and inter-atomic Coulomb interactions as well)[16] will, at most, modify the atomic levels (ϵ_s and ϵ_p)[8] deciding the band positions with respect to the vacuum level but will not alter the interatomic interactions ($V_{ll'm}$)[8] deciding the band widths, in a simple chain geometry before the s-p crossing has occurred. Without chemical bonding, low temperature environment is preferred to suppress thermal vibrations of adatoms and substrate atoms.

For a maximum stability of adatom positions, we may seek a scheme to allow chemical bonding with substrate atoms. We may adopt a regulated Si surface with unused dangling bonds being properly saturated with H atoms.[17] Adatoms are forced to form sp^3 orbitals that are exclusively used for covalent bonding with substrate Si atoms, and only the remaining s and p orbitals, not the full set of s and p orbitals, decide the chain properties. Therefore, even a basic conclusion such that Mg chains are semiconducting will undergo modification since the treatment has so far consistently assumed no forced sp^3 orbitals. The same chains may turn out to be metallic or semiconducting depending on the number of such sp^3 orbitals per adatom, or physically on the surface orientation and the substrate material. A further study is needed.

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[1]H.-S. Wong and Y. Taur, Tech. Dig. Int. Electron Devices Meet., 705 (1993), J.-R. Zhou and D. K. Ferry, IEEE Comp. Sci. Eng. **2**, 30 (1995).

[2]For example: D. M. Eigler and E. K. Schwiezer, Nature (London) (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).

[3]T. Yamada, J. Vac. Sci. Technol. B **15**, 1019 (1997); T. Yamada, J. Vac. Sci. Technol. A **15**, 1280 (1997); T. Yamada, Y. Yamamoto, and W. A. Harrison, J. Vac. Sci. Technol. B **14**, 1243 (1996).

[4]J. A. Stroscio, R. M. Feenstra, and A. P. Fein, J. Vac. Sci. Technol. A **5**, 838 (1987); J. A. Stroscio and R. M. Feenstra, *Methods of Experimental Physics,* Vol. 27, edited by J. A. Stroscio and W. J. Kaiser (Academic, San Diego, 1993), Chap. 4.

[5]P. W. Anderson, Phys. Rev. **109**, 1492 (1958); R. Landauer, Philos. Mag. **21**, 863 (1970); D. J. Thouless, Phys. Rev. Lett. **39**, 1167 (1977); P. W. Anderson, D. J. Thouless, E. Abraham, and D. S. Fisher, Phys. Rev. B **22**, 3519 (1980).

[6]W. Shockley, *Electrons and Holes in Semiconductors* (Van Nostrand, Princeton, 1950).

[7]J. C. Slater, *Quantum Theory of Matter* (McGraw–Hill, New York, 1968).

[8]W. A. Harrison, *Electronic Structure and Properties of Solids* (Freeman, San Francisco, 1980); Surf. Sci. **299/300**, 298 (1994); W. A. Harrison, Phys. Rev. B **24**, 5835 (1981).

[9]W. A. Harrison, Phys. Rev. B **31**, 2121 (1984).

[10]H. P. D. Lanyon and R. A. Tuft, Tech. Dig. Int. Electron Devices Meet, , 316 (1978); S. M. Sze, *Physics of Semiconductor Devices,* 2nd ed. (Wiley, New York, 1981).

[11]E. Buks, M. Heiblum, and H. Shtrikman, Phys. Rev. B **49**, 14 790 (1994); The mechanism is considered in A. L. Efros, F. G. Pikus, and G. G. Samsonidze, Phys. Rev. B **41**, 8295 (1990).

[12]C. Kittel, *Introduction to Solid State Physics,* 5th ed. (Wiley, New York, 1976).

[13]Usually flatter bands result in heavier effective masses, and therefore the transport is expected to degrade. In the context of conductance quantization in a one-dimensional system, however, the band shape does not have any influence upon the transport, owing to the cancellation of the electron velocity and the state density. For a full discussion, the contact to the electrodes has to be specified, which is beyond the scope of this article and left for a future study.

[14]A. P. Monkman, *An Introduction to Molecular Electronics,* edited by M. C. Petty, M. R. Bryce, and D. Bloor (Oxford, New York, 1995), Chap. 7 and references therein.

[15]The calculation shows that the dopant level moves into the band gap after the s-p band crossing, e.g., at $d_x = d_y = 3$ Å (figure not shown), which was also the case for K.

[16]W. A. Harrison and J. E. Klepeis, Phys. Rev. B **37**, 864 (1988); J. E. Klepeis and W. A. Harrison, J. Vac. Sci. Technol. A **6**, 1315 (1988).

[17]S. Watanabe, Y. A. Ono, T. Hashizume, Y. Wada, J. Yamauchi, and M. Tsukada, Phys. Rev. B **52**, 10 768 (1996).