Atomic wires and their electronic properties

Toshishige Yamada[a)]
ERATO Quantum Fluctuation Project, Edward L. Ginzton Laboratory, Stanford University, Stanford, California 94305-4085

(Received 12 January 1997; accepted 23 March 1997)

Atomic wire electronics are considered, where the band structure and the resultant Fermi energy are designed by manipulating the lattice constant. Using the tight-binding theory with universal parameters, it is shown that Si wires and arrays are metallic, Mg wires are insulating, and Mg arrays have metallic and insulating phases for infinitely large, isolated cases. Structures are of finite size, and electrodes are necessary for the applications. The finite size brings about discrete electron energy levels, and electrodes will charge or discharge the structure, reflecting the work function difference, so that even the basic electronic properties may be altered. The electrodes will cause further complications such as the energy level broadening, the Coulomb interaction through an effective capacitance, or the mode-selection resistance. When the contact satisfies certain conditions, a metallic wire is predicted to show two distinct $I-V$ patterns for small voltages. Depending on whether the highest occupied level is either partially or fully filled, the current starts to flow rapidly or does not flow until the voltage overcomes the next level, respectively. [S0734-211X(97)08704-0]

I. INTRODUCTION

Due to the recent progress in scanning tunnel microscope (STM) technology,[1] it is now becoming possible to manipulate atoms, or place them at desired positions. It is also routinely possible to prepare an atomically flat surface possessing two-dimensional periodicity. One such example is a reconstructed semiconductor surface. Using the STM atom manipulation technology, foreign atoms can be placed at the minima of the substrate periodic potential to form a one-dimensional atomic wire or a two-dimensional atomic array. After successful electronic isolation between the atomic structure and the substrate, electrons are confined within the structure and a low-dimensional electron system is obtained. The most attractive feature of this system is that we can manipulate the lattice constant and design the band structure and the resultant Fermi energy.[2]

The choice of a substrate providing both two-dimensional potential and electronic insulation is not trivial and we are studying the possibility of using a Si(100)2×1 reconstructed surface where the dangling bonds are saturated with hydrogen atoms.[3,4] Foreign atoms are placed at the minima of the periodic potential created by substrate surface atoms via van der Waals-like interparticle interaction, and an atomic structure such as a wire is created. The mechanical stability of such a wire may be an experimental concern: there might be a tendency for the wire atoms to deform the wire shape spontaneously, e.g., clustering or dimerization. This issue can be addressed with a phenomenological interparticle potential.[5,6] The potential includes the effects of kinetic, Coulomb, and exchange energies, and is featured in general by a hard core barrier for short distances, followed by a potential well that gives the natural separation of the particles, with an exponentially decaying tail for longer distances. In the present case, the separation among constituent wire atoms is chosen to be well beyond the natural distance and close to or inside the tail region, while the constituent atoms and the substrate atoms keep the natural distances, so that the wire will be mechanically stable.

The electronic properties of various atomic structures with Si or Mg atoms are studied[4] with the tight-binding calculation with universal parameters,[7] assuming that the structures are successfully isolated from the substrate and are infinitely large. It is shown that one-dimensional Si wires and two-dimensional Si arrays are metallic regardless of the lattice constant. One-dimensional wires of Si diatomic molecules are also metallic. All of these results reflect the fact that the highest occupied level is $3p$ and is partially filled in an isolated Si atom, and the Fermi energy is located in the $3p$-originating band. It seems quite difficult to obtain a semiconductor or an insulator with Si atoms having low-dimensional atomic structures. We thus need to use group II atoms such as Mg or Be atoms for a semiconductor or an insulator, since the s level is fully filled and the p levels are completely empty in these atoms, and their periodic structures will have a fully filled lower band and an empty upper band. According to the calculation, Mg wires are insulating or semiconducting, and two-dimensional Mg arrays have metallic and insulating phases depending on the lattice constant.

Metallic structures with partially filled bands will be conductive and insulating structures with completely filled bands will not be conductive, as long as the response to a small electric field is concerned. One may further expect that the metallic wires will exhibit an integer multiple of a quantum unit of conductance in the linear response regime since there are at most several one-dimensional modes (discrete momenta in the transverse directions and continuous momenta in the longitudinal direction) involved in the wire transport. In fact, the present situation is similar to that of mesoscopia,

a)Electronic mail: yamada@loki.stanford.edu

where the conductance quantization in small structures possessing at most a few modes has been verified theoretically and experimentally:[8] this is independent of the details of the dispersion (how the discrete energy levels form in the finite wire limit).

This naive view is subject to various modification.[9] First, electrodes have to be placed at the ends of the atomic structures for electronic measurements and device applications. Because of the possible work function difference between the wire and the electrodes, there would be a space-charge layer formation with an atomic scale, and the entire or part of the wire will be charged.[9,10] Once the wire is charged, the Coulomb interaction might be important in the transport, via the effective capacitance at the contact between the wire and the electrodes. Second, the number of atoms used in a wire is limited to an order of 10^1 as long as the structure is created, e.g., by placing foreign atoms one by one with STM atom manipulation technology. Due to the finite wire length, the discreteness of the energy levels, or a zero-dimensional effect (discrete momenta in the transverse and longitudinal directions) in the wire will be relevant.

The physical processes at the contact decide the relative importance of the Coulomb interaction and the discreteness of the energy levels.[9] When the particle exchange between the wire and the electrodes is extremely rare, an effective capacitance at the contact will be extremely small and the Coulomb interaction will be relevant. The longitudinal quantization effects are quite important, but the Coulomb interaction significantly modifies the discrete energy levels through the effective capacitance and even the spin degeneracy will be lifted. As the particle exchange rate increases, the Coulomb interaction is less and less relevant and the discrete energy levels are more and more broadened. When the particle exchange is extremely frequent, the electrons spread over the entire system and the effective capacitance is extremely large. The discrete nature of electron energy level is no longer present, and continuous bands appear.

With intermediate particle exchange, where the capacitance is large and the discrete nature of the electron levels is still relevant, we can expect two distinguished transport patterns reflecting how the electrons are accommodated in these discrete levels. When the highest occupied level of the wire is fully filled, the current does not flow without a voltage greater than the separation of the highest occupied and lowest unoccupied levels. Or, there is an offset voltage for the current onset. When the highest occupied level is partially filled, the current can flow even with a voltage smaller than the scale of quantized energy separation, but the differential conductance will not be infinite, but limited on the order of the quantum unit of conductance, due to the mode-selection resistance at the contact as in the mesoscopic systems.[8] Each time the Fermi energies in the electrodes cross a new wire level, there will be a sudden increase in current, resulting in stairlike $I-V$ characteristics.

In Sec. II, the band properties of the Si and Mg atomic structures are shown, using the tight-binding model with universal parameters. In Sec. III, physical processes at the contact between the wire and the electrodes are discussed. In Sec. IV, $I-V$ characteristics for metallic wires with two different fillings for the highest occupied level are shown, reflecting the momentum quantization along the wire. Summary and discussions are given in Sec. V.

II. ATOMIC WIRE ELECTRONICS-ELECTRONIC PROPERTIES OF Si AND Mg STRUCTURES

As long as the system has periodicity, we can find the following general behavior of the electronic states when changing the lattice constant without changing the lattice symmetry.[2] This general behavior can apply for all the lattice symmetry and dimensions.[11] When the lattice constant is large, the electrons are localized in each atom. The energy levels are in principle discrete and equivalent to those of isolated atoms, e.g., with an s level and three p levels in addition to the stable core levels that have rare gas configurations. As the lattice constant is reduced, the discrete energy levels have a finite width to form a band, because of an overlap of neighboring electron wave functions. At this stage, there are one lower state and three upper states, and each state can accommodate two electrons with spin up and down. If the lattice constant is further reduced, the band widths become so wide that one of the p-originating upper bands and the s-originating lower band touch. This is called band crossing. With further reduction in the lattice constant, there would be three possible cases, depending on the lattice symmetry and the dimension. (1) The touching upper band sticks to the lower band and they behave together. The resulting band structure is such that there are two lower states and two upper states, separated by a forbidden gap. Due to the change in accommodation number in the lower and upper bands, this will provide a mechanism for a metal-insulator transition. The usual diamond-structure Si crystal is semiconducting since the natural lattice constant happens to correspond to the one after band crossing. (2) The touching upper and lower bands repel each other to reopen a band gap after band crossing. There is no change in the number of states in the upper and lower bands, although the band gap is modulated with the lattice constant, resulting in no metal-insulator transition. This is the case for one-dimensional atomic wires. (3) The touching upper and lower bands overlap after band crossing, and the overlapped region is allowed, with each energy region corresponding to momenta in different directions. Thus, a large unified allowed energy region appears. This will also provide a mechanism for a metal-insulator transition. This behavior can be seen for two-dimensional arrays.

By using the tight-binding theory with universal parameters,[7] it is shown that Si wires are metallic and Mg wires are insulating regardless of the lattice constant.[4] Figures 1 and 2 show the band structure of Si and Mg wires for three different lattice constants, respectively. In principle, we can see the general behavior of the electronic states corresponding to (2). The only band gap reduces as the lattice constant is decreased, and vanishes at 2.7 Å for the Si wire and at 4.2 Å for the Mg wire. These lattice constants corre-

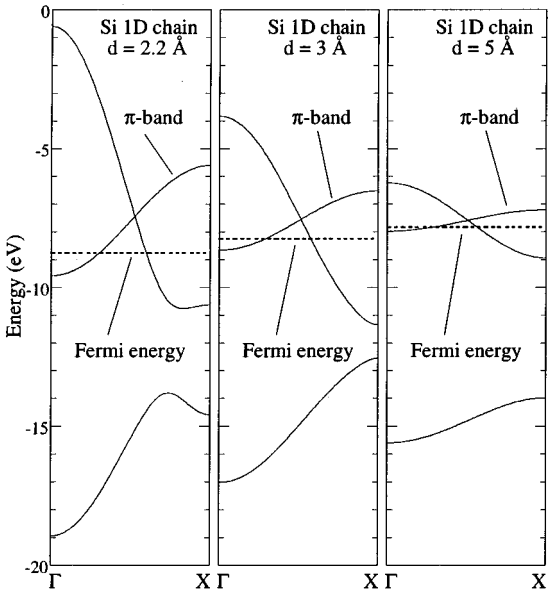

FIG. 1. Band structure of Si wire for selected lattice constants.

spond to band crossing. After this band crossing, a band gap reopens in both wires and we again have one state in the lower band and three states in the upper bands. The number of electrons that can be accommodated in the lower and upper bands remains the same. The major difference between Si and Mg is the number of electrons, or the Fermi energy position. In an isolated Si atom, the highest occupied level is $3p$ and is one-third filled. Since the number of states in the lower and upper bands remains the same regardless of the lattice constant, the Fermi energy always lies within the π band originating from two $3p$ levels normal to the wire and

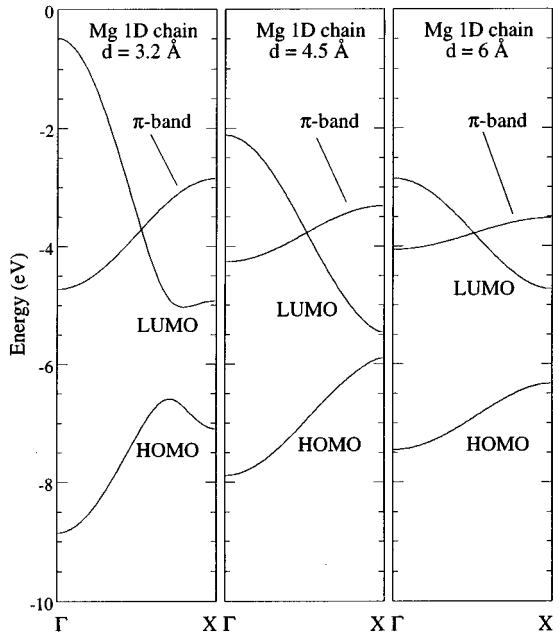

FIG. 2. Band structure of Mg wire for selected lattice constants.

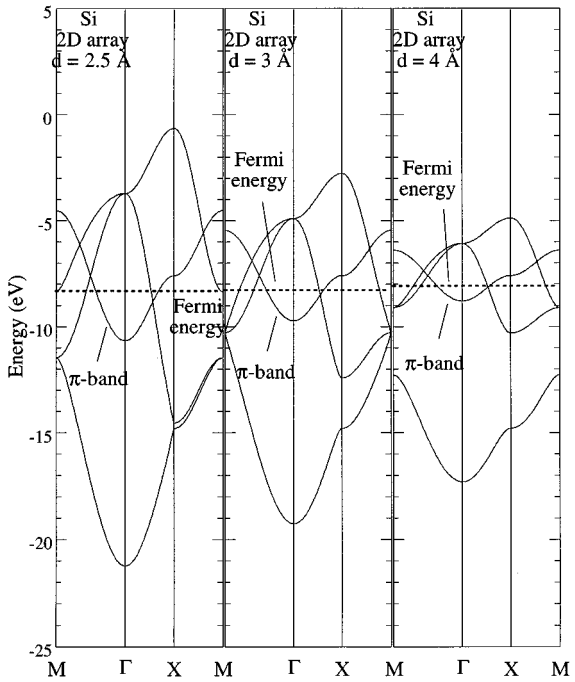

FIG. 3. Band structure of Si array for selected lattice constants.

this makes the Si wire metallic. In an isolated Mg atom, the highest occupied level is $3s$ and is fully filled while the $3p$ levels are empty. The lower band is always fully filled and the upper band is always completely empty, regardless of the lattice constant. This is why Mg wires are insulating or semiconducting.

Figure 3 shows that two-dimensional Si square arrays are metallic regardless of the lattice constant d, for the same mechanism as Si wires, where the Fermi energy is again within the π band. The only band gap disappears at $d = 3.4$ Å after band crossing, corresponding to the general behavior of (3) above, but the Fermi energy is always well above the band gap and its disappearance has no effect on the electronic properties. If we can create a Si diatomic molecule so that the highest occupied molecular level is fully filled, then a Si insulator would be possible by simply placing these Si diatomic molecules along a line. It turns out that this idea does not really work since the required interatomic distance is unreasonably small, less than the natural Si atom diameter, but it would work for C atoms.[4] Thus, it seems quite difficult to obtain an Si insulator having one- or two-dimensional lattice structures. Two-dimensional Mg square arrays have metallic and insulating phases depending on the lattice constant d, reflecting the disappearance of the band gap as shown in Fig. 4. For $d > 5.2$ Å, the lower band is fully filled and the upper bands are empty, resulting in an insulator. At $d = 5.2$ Å, the band crossing occurs and the band gap disappears. For $d < 5.2$ Å, the array is metallic since the upper and lower bands overlap and a large unified allowed energy region appears.

There is a pioneering experiment towards atomic wire electronics by Stroscio, Feenstra, and Fein.[12] They have ob-

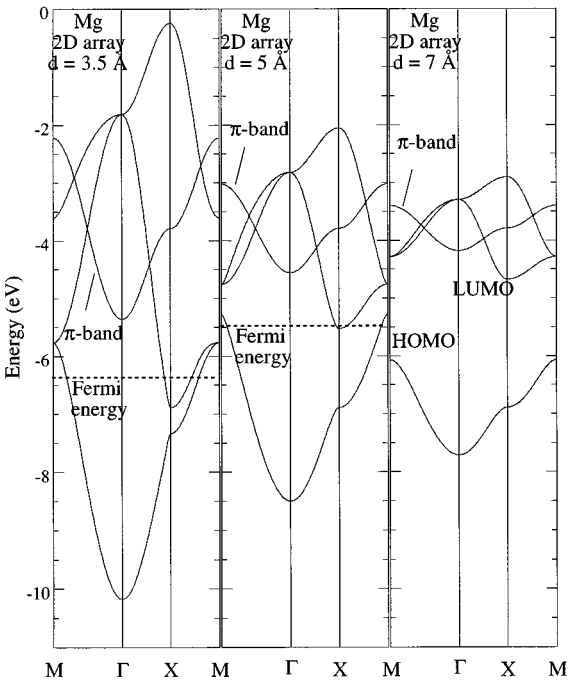

FIG. 4. Band structure of Mg array for selected lattice constants.

served a cleaved Si(111)2×1 surface with STM. The surface is characterized by a one-dimensional zig-zag wire of Si atoms with two basis atoms in a unit cell of 6.65 Å $\times$3.84 Å. Practically, we may think that one-dimensional wires consisting of dangling bonds with the lattice constant of 3.84 Å are placed in parallel, and the separation of wires are so large (6.65 Å) that interwire coupling is negligible. If the neighboring dangling bonds successfully couple in the wire direction and the electron wave spreads coherently over the entire wire, upper and lower bands are expected to form, which are separated by the only band gap. The electron filling is such that the lower band is fully filled and the upper band is empty,[12,13] so that the Fermi energy lies around the middle of the band gap and the wire is insulating. The positive substrate voltage (shifting the entire substrate bands downward with respect to the tip Fermi energy) is expected to image the upper empty band and the negative voltage the lower filled band. At each Si position, the electron wave function has a maximum for the lower band states and has a minimum for the upper band states (the strongest contrast at the Brillouin zone edge), thus creating π-phase shift difference between the two images of opposite bias polarity.

They have experimentally observed this π-phase difference in STM images for positive and negative substrate voltages. This experiment demonstrates a coherent wave-function overlap between neighboring atom sites in the wire direction even with a separation of $\sim$4 Å, much wider than the natural Si atom separation of 2.35 Å in the usual diamond-structure crystal. The overlap is still strong enough for electrons to form a band structure in spite of this large lattice constant. This is encouraging for the present situation. The lattice constant of an atomic structure has to be chosen well beyond the atom diameter to achieve a reasonable mechanical stability in order to avoid the possible deformation such as clustering or dimerization, but this may cause unwanted decoherence. Their experiment shows that the coherency is quite robust, and the decoherence would not be the case.

If we proceed to use foreign atoms to create an atomic structure, an appropriate substrate providing both periodic potential and electronic insulation has to be found. One possibility[14] is to use a Si reconstructed surface where the surface dangling bonds are saturated with hydrogen atoms to form a monohydrogen layer.[3,4] The dangling bonds are saturated so that the surface is expected to provide a two-dimensional van der Waals potential plane, and wire atoms are placed at the bottom of this potential without creating chemical bonds with the substrate atoms. The constituent wire atoms keep distances of well beyond their atom diameter, while the wire atoms and substrate atoms have distances corresponding to the natural separation.

There might be concern about the possible deformation such as clustering or dimerization after aligning wire atoms along a line, and this problem could be addressed with the help of a phenomenological interparticle potential.[5,6] The potential includes the effects of kinetic, Coulomb, and exchange energies and is featured by a hard core barrier for small distances, and a shallow potential well outside the barrier that gives the natural distances, followed by an exponentially decaying, slowly varying potential tail for large distances. The detail of the functional form depends on the kind of atoms. In the case of Si–Si interparticle-interaction, it is shown[6] that the potential minimum is at $\sim$2–2.5 Å (the natural diameter of the Si atom) with the depth of $\sim$2 eV, followed by an exponentially decaying tail for the distances larger than $\sim$3–3.5 Å with a negligible depth. The clustering of a Si wire will be relevant when the lattice constant is small, roughly corresponding to 2–2.5 Å. For the lattice constant to be larger than or equal to 3–3.5 Å, the deformation will be unlikely. The wire atoms are held by substrate atoms with the natural distance, while the wire atoms themselves keep distances well beyond the natural distance, so that the confining potential energy is much larger than a possible gain energy with deformation. No bands are half-filled in Si or Mg wires, and thus the Peierls transition[15] is not expected. The Peierls transition could be relevant if we were interested in wires that are half-filled, such as an alkali metal wire, but not here.

III. PHYSICAL PROCESSES BETWEEN WIRE AND ELECTRODES

For future atomic wire electronics, it is essential that technology be established to make a contact to electrodes that will be connected to batteries or to other atomic scale devices, and we need to clarify the physical processes of the contact at this stage. There will be particle exchange between the wire and the electrodes after contact, and if this occurs, the charge neutrality within the wire is not guaranteed, even in thermal equilibrium. (1) If the particle exchange through

the contact is extremely rare so that the electrons localize well inside the wire, the effective capacitance at the contact will be quite small and even the spin degeneracy will be lifted. The energy levels (renormalized to include the Coulomb interaction) are discrete, and the expectation value for the number of electrons in the wire is an integer. (2) If the contact allows some particle exchange, the electrons will not be strongly localized in the wire and the effective capacitance for this situation may be large. The spin degeneracy is not lifted, but the discrete nature of the allowed levels still prevails. The expectation value for the number of electrons is not necessarily an integer. (3) If the contact allows extremely frequent particle exchange, the electrons will spread over the entire system consisting of the electrodes and the wire, and the associated effective capacitance is huge, but the electron energy levels are no longer discrete. The particle exchange rate is determined by the physical processes around the contact, and is influenced by the separation between the atomic wire and the electrodes (barrier width), and the work function difference at the contact (barrier height). They can be independently tuned experimentally. As in macroscopic p-n junctions, it is expected that there are microscopic space-charge layers to absorb the work function difference between the wire and the electrodes.[10,11] The widths are estimated to be on the order of several atomic layers ($\sim$1 nm) for the energy difference of $\sim 10^0$ eV according to a formula $w \sim (2\epsilon V/eN_e)^{1/2}$ with $N_e^{1/3} \sim 10^9$ m^{-1} and $\epsilon/\epsilon_0 \sim 10^1$.

We need to think of the finite-length effects of a wire. The band width W of the wire is determined by the lattice constant d and is a decreasing function of d until the bands cross.[4,7] W does not depend very much on the number of atoms N as long as $N \gg 1$, and the average level separation is given by W/N.[11] These energy levels in principle correspond to the modes whose envelope functions are standing waves within the wire, and are well approximated with this picture. The highest and lowest states correspond to infrared and ultraviolet cutoff states in the wire structure, respectively. Typical $W(d)$ values are such that a Si metallic wire has a $W=5$ eV for $d=4$ Å, and a Mg semiconducting wire has a $W=1.5$ (valence) and 2.7 eV (conduction) for $d=5$ Å,[4] so that the level separation is on the order of 10^{-1} eV for $N \sim 10^1$. If fully filled, the Fermi energy, ζ, lies in the middle of the highest-occupied and lowest-unoccupied levels. If partially filled, ζ lies at the highest occupied level. The electron filling can be changed by tuning the wire length and designing electrodes as shown below.

Figure 5(a) schematically shows the energy band alignment in equilibrium before contact, assuming that the electrode work function χ_e is greater than the wire work function χ_w. Energy lines for the opposite situation can be obtained with a vertical flip of the energy figures. ζ_e and ζ_w are the Fermi energies of the electrodes and the wire measured from the band bottom or the lowest level, respectively (both excluding the core levels). ϕ_e and ϕ_w are electrostatic energies for the electrodes and the wire, respectively. As is different from the usual macroscopic p-n junctions, the electrostatic

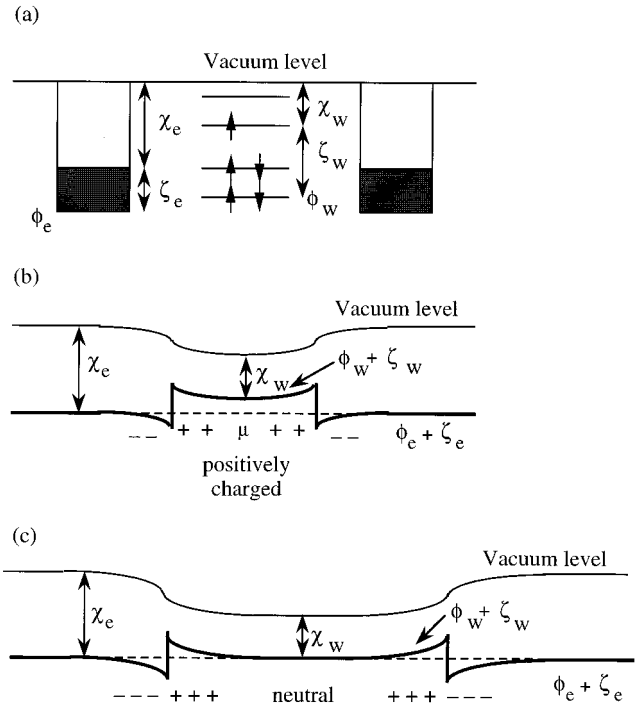

FIG. 5. Physical processes at contact between wire and electrodes: (a) Energy alignment before contact; (b) contact to short atomic wire; (c) contact to long atomic wire.

energy depends logarithmically on the distance from the center axis of the wire, and the energy lines should be understood as results of the appropriate averaging weighted with relevant electron wave functions.

After contact, electrons will spill out from the wire to the electrodes due to the work function difference $\chi_e > \chi_w$. Figures 5(b) and 5(c) indicate the equilibrium energy alignment for short and long wires, respectively. The thick lines are the summation of the electrostatic energy ϕ and the Fermi energy ζ, and the thin lines are vacuum levels. The electrochemical potential μ,[16] with a broken line, equals $\phi_e + \zeta_e$ deep inside the electrodes. Discrete energy levels (not shown) will be formed under the influence of ϕ, as in the case of an inversion channel with a triangular potential in a macroscopic heterojunction. If $\phi + \zeta - \mu$ is positive, that point is positively charged, and if negative, negatively charged. The discontinuity in electrostatic energy $(\phi_w + \zeta_w) - (\phi_e + \zeta_e)$ at the contact equals the work function difference $\chi_e - \chi_w$.[10,16] If the wire is so short that the space charge layers at both ends touch as shown in Fig. 5(b), the charge neutrality is broken over the entire wire, and the electron filling for the discrete energy levels is no longer equivalent to that for an isolated wire. If the wire is long or the discontinuity in $\phi + \zeta$ is small so that the space-charge layers never touch, the charge neutrality holds with $\phi_w + \zeta_w = \mu$ in the middle as in Fig. 5(c). The electron filling in the middle is the same as that in an isolated wire, and this limit provides a situation of interacting Fermions described by the Tomonaga–Luttinger model.[17]

It has to be emphasized that there is certainly a case that

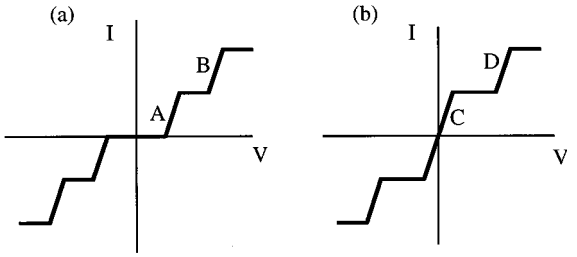

FIG. 6. Expected $I-V$ characteristics with intermediate particle exchange at contact: (a) fully filled and (b) partially filled cases.

the electron filling in the wire with electrodes is completely different from that of the wire without electrodes as in Fig. 5(b). In an extreme situation, the electronic nature of the wire would be altered drastically, such that a metallic wire without electrodes will be insulating with electrodes or vice versa. In order to observe that a Si wire is metallic and a Mg wire is insulating, we need to make the wires long enough, much longer than the space charge layer width, or design the electrodes so that the work function difference will be minimized as in Fig. 5(c). The longer wires have their electronic identity while the shorter wires do not, and it is worth noticing this trivial, but important point.

IV. EXPECTED *I–V* CHARACTERISTICS WITH INTERMEDIATE PARTICLE EXCHANGE

With intermediate particle exchange, with $\chi_e \sim \chi_w$, we expect that the associated effective capacitance is large and the discreteness of energy levels is still relevant. Then, there will be two distinct patterns for metallic wire transport: the electrons are less likely to flow for a fully filled case and more likely for a partially filled case, where the maximum differential conductance is limited by the mode-selection process at the contact. The expected $I-V$ patterns are schematically shown in Figs. 6(a) and 6(b) for fully and partially filled cases, respectively. For the fully filled case, the current will flow only when the applied voltage overcomes the separation of the discrete energy levels as in portion A, while for the partially filled case, the current will flow with an infinitesimal voltage as in portion C. The typical energy separation is on the order of 10^{-1} eV for an atomic wire with 10^1 atoms with a separation of 10^0 Å, and this gives a rough scale for the expected offset voltages. When a finite voltage is applied, the electrode Fermi energies in the source and drain split to support it. Every time the electrode Fermi energies cross a new wire level, it creates a sudden increase in current by forming steps in the $I-V$ characteristics as shown in portions B and D. The current onsets have a finite gradient due to the mode-selection process at the contact. As is often pointed out in mesoscopia, such mode selection at the contact causes a finite conductance even though the transmission coefficient is unity, and we will observe the quantum unit of conductance (or its integer multiple).[8] With this inherent effect, the differential conductance of the current onset cannot be infinite experimentally, but limited to be on the order of the quantum unit of conductance.

The current value at a step is determined by either the electron group velocity corresponding to the mode of interest or the transmission coefficient.[18,19] Since one mode (a zero-dimensional mode where the momentum along the wire is also quantized) creates one discretized current independent of the voltage in the lowest order approximation, we will have stairlike $I-V$ patterns. This stairlike shape is a general feature of the expected $I-V$ characteristics and is independent of the details of the calculation model.

In the infinite wire limit, we can mathematically show that the quantum unit of conductance will be recovered, regardless of the boundary condition, which is a restatement of the usual cancellation of the electron state density and the electron group velocity.[8] It has to be emphasized that this result is independent of the details of the dispersion or how the discrete energy levels have been formed in the original finite wire, and applies to quite general cases with a few modes, as is established in mesoscopia.[8] The current is proportionate to the voltage in this limit simply because the number of modes participating in the transport is proportionate to the applied voltage, due to the continuous distribution of modes in the relevant energy region. This prediction is at least not contradictory to the experimental findings of the quantization of conductance in various metallic wire structures with atomic dimensions,[20] but not yet exactly verified experimentally. In fact, each studied geometry is not quite the one-dimensional atomic wires discussed here. Second, we cannot completely exclude the possibility that they have observed, e.g., bimodal transmission in the diffusive regime.

V. SUMMARY AND DISCUSSIONS

Various atomic structures with Si and Mg atoms are studied theoretically, and it is shown that Si wires and arrays are metallic, Mg wires are insulating, and Mg arrays have metallic and insulating phases. The calculation neglects the effects from the substrate, but they will not change the above results qualitatively.[4] The electronic properties of wires cannot be discussed without specifying the electrodes, especially when the wire is short, because of the physical processes at the contact. The particle exchange rate at the contact determines the relative importance of the Coulomb interaction and the level broadening effect. With intermediate particle exchange along with $\chi_e \sim \chi_c$, depending on whether the highest occupied level is fully filled or partially filled, there would be differences in the $I-V$ characteristics for metallic wire transport. An offset voltage is required for a current onset for the former, while an immediate current onset is expected for the latter, with a finite differential conductance on the order of the quantum unit of conductance. Each time the Fermi energies in the electrodes cross a new wire level with voltage, a step in the $I-V$ characteristics results.

Lang has already discussed a special situation on how space charge layers form in Ref. 21 with a first-principle calculation. He studied the electronic properties of an adatom on a metallic surface, and assumed that the Fermi energy of the adatom aligned to that of the metallic surface. The adatom was either filled or depleted with electrons, depending

on the difference of the original work functions before contact. The discussion here is consistent with this if the adatom is regarded as the shortest wire in Fig. 5(b).

Lang studied the transport of an atomic wire with the first principle method in Ref. 22, where Al atomic wires with one or three atoms showed a larger conductance than that with two atoms. He assumed that the coupling of the wire atoms to the electrodes was so strong that the wire state densities were no longer discrete as in an isolated system, but had a significant width and overlap, showing some peaks only. This corresponds to a situation between the intermediate and extremely frequent particle exchange discussed above. Even in this case, there was a noticeable difference in transport properties between a two-atom wire, and one- and three-atom wires, and the current article is consistent with his result. In fact, if the Al wire is isolated, the parallel p state along the Al wire is modified more than the perpendicular p states because the $V_{pp\sigma}$ coupling is stronger than the $V_{pp\pi}$ coupling as discussed in Ref. 7. The highest occupied molecular level therefore originates from this parallel p state and is not degenerate, so that the highest occupied level is partially filled in one- and three-atom wires while it is fully filled in a two-atom wire. The former wires must have a better transport than the latter according to the view here, and his results showed it.

It is pointed out that there would be a Fermi energy pinning mechanism at the surface due to the surface states[16] for a macroscopic junction, and the discontinuity in the electrostatic potential was not always a difference of two work functions. Such surface states do arise at the contact edge, but only when the lattice constant is so short such that the band crossing occurs, resulting in the Shockley's surface states.[11,23] We need to avoid such short lattice constants in order to achieve mechanical wire stability, and both requirements are consistent. Alternatively, the surface contamination or the existence of foreign atoms on the surface would bring about these surface states, but they are unlikely under a ultrahigh vacuum STM environment, and the Fermi energy pinning through this route will not practically occur, either.

For electronics applications, there are some possible directions. One is to design devices making use of the Coulomb blockade effects with extremely small capacitances that can easily be obtained in the current atomic dimensions. Another is to create various junctions of different wires, where the Coulomb interaction will be suppressed by selecting a large-capacitance contact. This will lead to atomic wire electronics, to design materials with desired electronic properties by changing the atom arrangement, and employ the same device ideas in current semiconductor technology. For example, a Si wire is metallic and a Mg wire is insulating. Then, is the series junction of these two wires equivalent to a macroscopic metal-semiconductor junction showing rectifying characteristics? Does the junction structure of a metallic two-dimensional Mg array and a semiconducting Mg wire work as a metal-semiconductor junction? How can we dope an intrinsic semiconducting Mg wire, and how can we make a p-n junction? Any possibility for the creation of light-emitting diodes? These points are left for future studies.

ACKNOWLEDGMENTS

The author is especially indebted to Professor W. A. Harrison for the discussions of band calculations and Professor M. Heiblum for the discussions of Coulomb interaction.

[1]For example: D. M. Eigler and E. K. Schweizer, Nature (London) **344**, 524 (1990); J. A. Stroscio and D. M. Eigler, Science **254**, 1319 (1991); I.-W. Lyo and Ph. Avouris, Science **253**, 173 (1991); D. M. Eigler, C. P. Lutz, and W. E. Rudge, Nature (London) **352**, 600 (1991); H. J. Hamin, S. Chiang, H. Birk, P. H. Guethner, 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**, 1437 (1993); H. Uchida, D. Huang, F. Grey, and M. Aono, Phys. Rev. Lett. **70**, 2040 (1993); Ph. Avouris, I.-W. Lyo, and Y. Hasegawa, J. Vac. Sci. Technol. A **11**, 1725 (1993); C. T. Salling and M. G. Lagally, Surf. Sci. **265**, 502 (1994).

[2]In the early time of band calculations, a gedanken experiment was often performed: plot the band widths as a function of lattice constant ranging from infinite to finite values, and clarify how bands originate from atomic levels, e.g., W. Shockley, *Electrons and Holes in Semiconductors* (Van Nostrand, Princeton, 1950) or J. C. Slater, *Quantum Theory of Matter*, (McGraw-Hill, New York, 1968). It has been recognized since then that the band structure can be modified by manipulation of the lattice constant. Due to the current development of atom manipulation technology, it is becoming possible to pursue this idea and proceed to atomic wire electronics.

[3]T. Yamada, Y. Takiguchi, D. Huang, and Y. Yamamoto, *Atomic Wire Circuit Network and Method*, US Patent 1995, pending; D. Huang and Y. Yamamoto, Jpn. J. Appl. Phys. **35**, 3734 (1996).

[4]T. Yamada, Y. Yamamoto, and W. A. Harrison, J. Vac. Sci. Technol. B **14**, 1243 (1996); T. Yamada and Y. Yamamoto, Phys. Rev. B **54**, 1902 (1996).

[5]For potential between closed-shell atoms, R. G. Gordon and Y. S. Kim, J. Chem. Phys. **56**, 3122 (1972).

[6]For extention to open-shell atoms, W. A. Harrison and R. Sokel, J. Chem. Phys. **65**, 379 (1976).

[7]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); **31**, 2121 (1984).

[8]C. W. J. Beenakker and H. van Houten, in *Solid State Physics*, edited by Ehrenreich and D. Turnbull (Academic, San Diego, 1991), Vol. 44 and references therein.

[9]T. Yamada, J. Vac. Sci. Technol. A (to be published).

[10]S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981).

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

[12]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, in *Methods of Experimental Physics*, edited by J. A. Stroscio and W. J. Kaiser (Academic, San Diego, 1993), Vol. 27, Chap. 4.

[13]K. C. Pandey, Phys. Rev. Lett. **47**, 1913 (1981).

[14]There is another idea, which is to allow the foreign atoms to create chemical bonds with the substrate atoms by choosing an appropriate combination of the foreign atoms and substrate atoms with a suitable crystal orientation, requiring the electronic states to be localized within wires (or arrays) having a energy spectrum well inside the surface band gap of the substrate, S. Watanabe, Y. A. Ono, T. Hashizume, Y. Wada, J. Yamauchi, and M. Tsukada, Phys. Rev. B **52**, 10 768 (1996). It has to be emphasized that the band structure and the Fermi energy are generally different from those of an isolated wire. The wire and the substrate are unified electronically, and all the physical properties have to be designed for the entire system. For example, the creation of a second wire or the small fluctuation in substrate doping may alter the properties of the original wire completely. However, this route may open the door to higher temperature operation due to the excellent mechanical stability of the wire.

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

[16]J. Bardeen, Phys. Rev. **71**, 717 (1947).
[17]S. Tomonaga, Prog. Theor. Phys. **5**, 544 (1950); J. M. Luttinger, J. Math. Phys. (N.Y.) **4**, 1154 (1963).
[18]For the group velocity picture, see H.-F. Chueng, Y. Gefen, E. K. Riedel, and W.-H. Shih, Phys. Rev. B **37**, 6050 (1988;), and for the transmission picture, see Y. Imry, in *Directions in Condensed Matter Physics*, edited by G. Grinstein and G. Mazenko (World Scientific, Singapore, 1986) Vol. 1; R. Landauer, Z. Phys. B **68**, 217 (1987); M. Büttiker, Phys. Rev. Lett. **57**, 1761 (1986).
[19]How the group velocity and the transmission pictures are related to give a consistent, unified description for the current magnitude is left for future study. The general shape of the I–V characteristics is steplike, and a detailed model will just address how much the current and voltage steps are, respectively, in the limit of intermediate particle exchange. Those details are not of interest here.
[20]U. Landman, W. D. Luedtke, N. A. Burnham, and R. J. Colton, Science **248**, 454 (1990); C. J. Muller, J. van Ruitenbeek, and L. J. de Jongh, Phys. Rev. Lett. **69**, 140 (1992); L. Olesen, E. Laegsgaard, I. Stensgaard, F. Besebbacher, J. Schiøtz, P. Stoltze, K. W. Jacobsen, and J. K. Nørskov, Phys. Rev. Lett. **72**, 2251 (1994); J. M. Krans, J. M. Van Ruitenbeek, V. V. Fisun, I. K. Yanson, and L. and J. De Jongh, Nature (London) **375**, 767 (1995); J. L. Costa-Krämer, N. García, P. García-Mochales, and P. A. Serena, Surf. Sci. **342**, L1144 (1995); J. I. Pascual, J. Méndez, J. Gómez-Herrero, A. B. Baró, N. Garcia, Uzi Landman, W. D. Luedtke, E. N. Bogachek, and H.-P. Cheng, Science **267**, 1793 (1995).
[21]N. D. Lang, Phys. Rev. Lett. **56**, 1164 (1986).
[22]N. D. Lang, Phys. Rev. B **52**, 5335 (1995).
[23]W. Shockley, Phys. Rev. **56**, 317 (1939).