Transport properties along a finite-length atomic chain

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

(Received 26 September 1996; accepted 9 December 1996)

We study the electron transport properties of a finite-length atomic chain created on an insulating substrate. Discrete energy levels are formed due to the finite length, and they are expected to show some trace in the $I-V$ characteristics that are not predicted by an infinite chain model. Practically, electrodes are necessary for an electrical measurement but they cause complications: energy level broadening in the chain, chain charging due to the work function difference, Coulomb interaction through an effective capacitance, and mode selection resistance. If certain conditions are satisfied, depending on whether the highest occupied level is fully or partially filled in the chain, there is, respectively, an offset voltage for the current onset corresponding to the discrete energy separation, or the current rises rapidly for an infinitesimal voltage with a finite differential conductance on the order of quantum unit of conductance. © *1997 American Vacuum Society.*
[S0734-2101(97)51903-8]

I. INTRODUCTION

As a result of recent progress in atom manipulation technology, it is now becoming possible to place atoms along a line on insulating substrates by using a scanning tunnel microscope (STM) tip as tweezers.[1] The choice of such substrates is not trivial and we have proposed the use of a Si reconstructed surface where the surface dangling bonds are saturated with hydrogen atoms.[2] Atoms are placed at the minima of periodic potential created by substrate surface atoms via van der Waals interaction. Since the band structure and the Fermi energy are controlled by changing the lattice constant of an atomic chain, we can design the electronic properties and obtain the desired material. We have theoretically predicted that a Si chain and an alternating GaAs chain are always metallic, while a Mg chain is insulating or semiconducting with a variable band gap, in the limit of infinite chain.[3]

There is a realistic limit for the possible length of such atomic chains if we place atoms one by one with a STM tip. The finite length leads to the discrete energy levels in the chain, and this may give some trace in the $I-V$ characteristics that will not be predicted by an infinite chain model. However, there are some experimental complications. Electrodes are mandatory for an electrical measurement. Their existence will broaden the electron energy levels. There will be space-charge layers with atomic dimensions at the contact as a result of the work function difference between the chain and the electrodes, and the chain may be charged. When particle exchange between the chain and the electrodes is extremely infrequent, an effective capacitance at the contact will be extremely small and the Coulomb interaction will be relevant. Such a small capacitance may lift the electron spin degeneracy. Under a certain situation such that the Coulomb interaction is irrelevant and the discrete energy levels are not broadened significantly, we can expect two distinguished transport patterns, reflecting the discrete nature of the levels depending on the electron filling. If the highest occupied level 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. If the highest occupied level is partially filled, the current can flow even with voltage smaller than the scale of quantized energy separation, but the differential conductance will be limited on the order of the quantum unit of conductance due to the mode selection at the contact as is the case in the mesoscopic systems. Each time the Fermi energies in the electrodes cross a new chain level, there is a sudden increase in current, and we will have stairlike $I-V$ characteristics.

In Sec. II, physical processes at the contact between the chain and the electrodes are discussed. In Sec. III, $I-V$ characteristics for two different fillings are shown. The summary and discussion are given in Sec. IV.

II. PHYSICAL PROCESSES BETWEEN CHAIN AND ELECTRODES

Figure 1(a) shows the schematic band diagram for an infinite chain. The band width W of the chain is determined by the lattice constant d and is an increasing function of d until the band lines cross.[4,5] 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.[4] Typical $W(d)$ values are such that a Si metallic chain has $W=5$ eV for $d=4$ Å, and a Mg semiconducting chain has $W=1.5$ eV (valence) and 2.7 eV (conduction) for $d=5$ Å,[3] so that the level of separation is on the order of 10^{-1} eV for $N \sim 10^{1}$. In an isolated finite chain, the uppermost electrons lie at an energy similar to its counterpart of an infinite chain, but the highest occupied level is either fully filled or partially filled as shown in Figs. 1(b) and 1(c), respectively. The filling is decided by the number of electrons in the chain, which is an integer in an isolated chain, and by how the quantized levels are formed. If fully

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

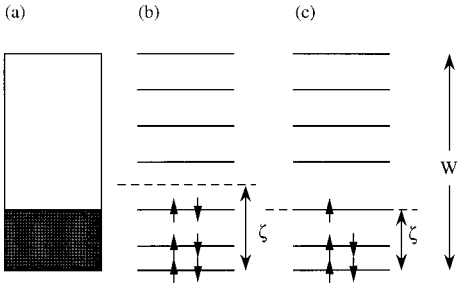

FIG. 1. Electron energy states of a metallic chain: (a) infinitely long chain; (b) finite chain with fully filled highest occupied level; (c) finite chain with partially filled highest occupied level. Broken lines indicate the Fermi energy ζ. W is the bandwidth.

filled, the Fermi energy, denoted by ζ and shown with a broken line in Fig. 1, lies in the middle of the highest-occupied and lowest-unoccupied levels. If partially filled, ζ lies at the highest occupied level. The negative electron charge compensates the positive nuclear charge, and the chain remains neutral in this isolated case.

When the chain is not isolated and is coupled to, e.g., electrodes for an electrical measurement so that there will be particle exchange between the chain and the environment, the charge neutrality within the chain is not guaranteed even in thermal equilibrium. The spin degeneracy is not assumed to be lifted throughout this article, but will be in a certain situation due to Coulomb interaction through an effective capacitance at the contact as in the case of a quantum dot. This is closely related to the nature of the contact between the chain and the electrodes. (1) If particle exchange through the contact is extremely infrequent so that the electrons are strongly localized inside the chain, the expected capacitance will be quite small and 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 chain is an integer. (2) If the contact allows some particle exchange, the electrons will not be strongly localized in the chain and the effective capacitance for this situation may be large. The spin degeneracy and the discrete nature of the allowed levels are still relevant. 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 electrodes and the chain, and the associated effective capacitance is huge, but the electron energy levels are no longer discrete. The situation discussed in this article relates to (2), although at this stage there is no quantitative prescription on how to realize it experimentally. The particle exchange rate is determined by the physical processes at the contact, and is influenced by the distance between the atomic chain and the electrodes, as well as the work function difference.

As in macroscopic p-n junctions, it is expected that there are microscopic space-charge layers to absorb the work function difference between the chain and the electrodes.[6] The widths are estimated to be on the order of several atomic

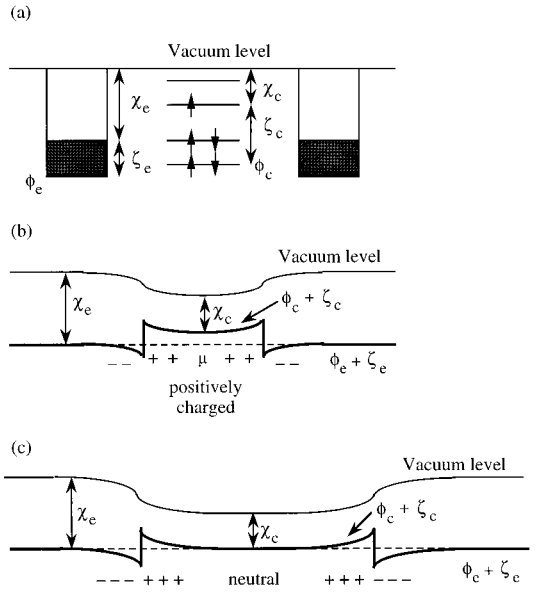

FIG. 2. Effects of contact in equilibrium: (a) energy band in the electrodes and quantized energy levels in the chain before contact; (b) space charge formation for the short chain after contact; (c) space charge formation for the long chain after contact. Broken lines indicate the electrochemical potential μ. ζ is the Fermi energy, χ is the work function, and ϕ is the electrostatic energy.

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 $\epsilon/\epsilon_0 \sim 10^1$ (in this atomic scale, the dielectric function represents the effects of many-body interaction[5] but, currently, we have no data for this value and employ a typical value for semiconductor atoms in the usual crystal structure).

Figure 2(a) schematically shows an energy band alignment in equilibrium before the chain and the electrodes make contact. This example shows a situation where the electrode work function χ_e is greater than the chain work function χ_c. Energy lines for the opposite situation can be obtained with a vertical flip of the energy figures. ζ_e is the Fermi energy of the electrodes measured from the bottom of the band and ζ_c is the Fermi energy of the chain measured from the lowest level (both excluding the core levels). ϕ_e and ϕ_c are electrostatic energies for the electrodes and the chain, respectively. Different from usual macroscopic p-n junctions, the electrostatic energy depends logarithmically on the distance from the center axis of the chain in this one-dimensional system. It should be understood that the electrostatic energy lines are results of appropriate averaging weighted with relevant electron wave functions. The energies align with respect to the vacuum level, which is constant before contact.

After contact, electrons will spill out from the chain to the electrodes in this example, due to the work function difference $\chi_e > \chi_c$. Figures 2(b) and 2(c) indicate the equilibrium energy alignment for short and long chains, respectively, after contact. The thick lines are the summation of the electrostatic energy ϕ and the Fermi energy ζ, and thin lines are vacuum levels. Due to the thermodynamics requirement, the electrochemical potential μ, shown with broken lines, must

be constant in equilibrium[7] and is equal to $\phi_e+\zeta_e$ deep inside the electrodes. If ζ_c remains the same before and after contact, the charge neutrality is preserved in the middle of the chain since the electron filling is unchanged there. If not, there is an exchange of electrons even in the middle, and the entire chain is charged. Whether the chain is positively or negatively charged depends on the respective magnitudes of ζ_c before and after contact, and this can be best visualized by plotting $\phi_c+\zeta_c-\mu$ as a function of position. If this value is positive, that position is positively charged, and if negative, the reverse is true. The same argument applies to the electrodes. The discontinuity in energy $(\phi_c+\zeta_c)-(\phi_e+\zeta_e)$ at the contact equals the work function difference $\chi_e-\chi_c$, but is not necessarily a potential barrier height at the contact seen by electrons participating in transport. This is similar the Schottky barrier not being an exact barrier height for transport electrons in a macroscopic metal–semiconductor junction.

If the chain is so short that the space-charge layers at the both ends touch as shown in Fig. 2(b), the charge neutrality is broken over the entire chain, and electron filling for the discrete energy levels is no longer equivalent to that for an isolated chain or, equivalently, ζ_c changes before and after contact. This is partly due to the change in the number of electrons in the chain. Another possible factor, assumed to be irrelevant here [an intermediate particle exchange rate as explained in (2) above], but probably important in practice, is the electron energy renormalization due to Coulomb interaction. The breakdown in charge neutrality can be seen as a nonzero value of $\phi_c+\zeta_c-\mu$ in the chain.

If the chain is long enough to have a significant length of charge-neutral region around its middle, or the discontinuity in $\phi+\zeta$ at the contact is so small that the space-charge layer widths are really restricted within a couple of atoms, the energy alignment will be as shown in Fig. 2(c). The effects of the space-charge layers are negligible around the middle of the chain and we thus have the relation $\phi_c+\zeta_c=\mu$. Electron filling in the middle of the chain is the same as that in the isolated chain. This limit corresponds to the situation of interacting Fermions described by the Tomonaga–Luttinger model.[8]

In the special case of $\chi_e\sim\chi_c$, there is little discontinuity in energy at the contact for electrons at the highest occupied level and the chain remains almost neutral. If a tapered structure, for example, is successfully created at the edge of the electrodes, a gradual smooth transition of electronic properties from the chain to the electrodes is achieved. Then, all the electron waves that match the chain modes can transmit although those that do not match are reflected back to the source side, and all the transmitted waves are absorbed in the drain side. The number of electrons in the chain remains the same before and after contact to the electrodes is established. In the limit of extremely frequent particle exchange between the chain and the electrodes with $\chi_e=\chi_c$, the energy levels overlap significantly to form a unified band and we can expect that an infinite chain model will well describe the electronic properties, and that the $I-V$ characteristics will follow that of an infinite chain. In the limit of extremely infrequent particle exchange, the Coulomb interaction will lift the spin degeneracy where the energy levels are discrete, and the Coulomb blockade effect will show a trace of $I-V$ characteristics. In the intermediate limit of these two, we may expect that the spin degeneracy is not lifted and the discrete nature of the energy levels is still relevant, for which we predict $I-V$ characteristics.

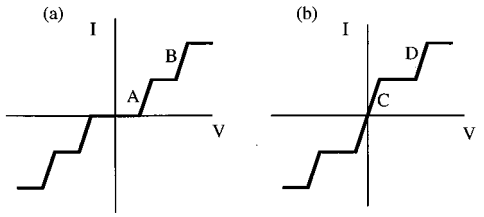

FIG. 3. Expected $I-V$ characteristics: (a) fully filled case and (b) partially filled case.

III. EXPECTED *I–V* CHARACTERISTICS

With an intermediate particle exchange rate with $\chi_e\sim\chi_c$, we expect that the associated effective capacitance is large and the discreteness of energy levels is still relevant, as discussed above. Then, the electrons are less likely to flow for a fully filled case and more likely to 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. 3(a) and 3(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, whereas 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 chain with 10^1 atoms with a separation of 10^0 Å, and this gives a rough scale for 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 chain level, the new level creates a sudden increase in current by forming a step in $I-V$ characteristics as shown in portions B and D. A simultaneous participation of two levels is possible if the upper and lower levels cross the electrode Fermi energies at the same time, within this present picture of irrelevant Coulomb interaction. The current onsets A, B, C, and D in Figs. 3(a) and 3(b) have a finite gradient due to the mode selection process at the contact. As is often pointed out in mesoscopic systems, 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).[9] With this inherent effect, the differential conductance of the current onset cannot be infinite experimentally, but is limited to be on the order of the quantum unit of conductance, and this situation is shown schematically in Fig. 3.

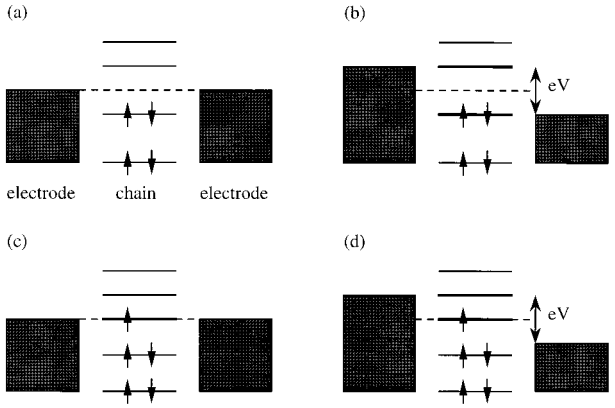

FIG. 4. Energy alignment for electrodes and chain: (a) $V=0$ and (b) $V\neq 0$ for fully filled cases, and (c) $V=0$ and (d) $V\neq 0$ for partially filled cases. Thick lines indicate the modes involved in transport.

The $I-V$ characteristics are clearer in the schematic presentation of energy alignment for various bias V in Fig. 4: (a) $V=0$ and (b) $V\neq 0$ for fully filled cases, and (c) $V=0$ and (d) $V\neq 0$ for partially filled cases, corresponding to A, B, C, and D in Fig. 3, respectively. The chain level near the electrode Fermi energy is absent in Fig. 4(a), and present in Fig. 4(c), and this explains the $I-V$ pattern difference of portions A and C at small voltages. There is a first current step B in the $I-V$ pattern for the fully filled case when the voltage is increased and the chain levels shown with thick lines are involved in the transport as in Fig. 4(b). The second current rise D for the partially filled case is due to the newly participating chain level indicated with a thick line in Fig. 4(d). The current is expected to show a further step each time the electrode Fermi energies cross a new chain level at higher voltages.

The current value at a step is determined by either the electron group velocity corresponding to the mode of interest[10] or the transmission coefficient.[11] Since one mode creates one discretized current independent of the voltage in the lowest order approximation, we will have stairlike $I-V$ patterns as shown in Fig. 3. Taking the limit of the infinite chain, we have an infinite number of infinitesimally small steps, recovering the quantum unit of conductance mathematically. In fact, the discrete energy separation is infinitesimally narrow in the chain and the usual cancellation of the electron state density and the electron group velocity prevails. 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 is at least not contradictory to experimental findings of the quantization of conductance in various metallic wire structures with atomic dimensions,[12] but it is not yet exactly verified either. In fact, the geometry studied in Ref. 12 is not quite the one-dimensional atomic chains discussed here. Also, we cannot completely exclude such possibility that they have observed, e.g., bimodal transmission in the diffusive regime.

IV. SUMMARY AND DISCUSSION

The effects of the finite length of an atomic chain on electron transport properties are discussed. Because of the finite length, the electrons form discrete energy levels in an isolated chain. The electrodes have to be placed for an electrical measurement; this introduces interaction with the environment. The particle exchange rate between the chain and the electrodes determines whether the discreteness of the levels and Coulomb interaction are relevant in the chain or not. With an intermediate particle exchange rate with $\chi_e \sim \chi_c$, depending on whether the highest occupied level is fully filled or partially filled, there would be differences in $I-V$ characteristics. An offset voltage is required for a current onset for the former, whereas an immediate current onset is expected for the latter, with a finite differential conductance on the order of the quantum unit of conductance. The typical energy separation is on the order of 10^{-1} eV for an atomic chain with 10^1 atoms with a separation of $\sim 10^0$ Å, and roughly gives an estimation for the offset voltage. Each time the Fermi energies in the electrodes cross a new chain level, a step in the $I-V$ characteristics results. The current magnitude for each step is critically dependent on the physical processes at the contact.

Lang has already discussed how space-charge layers form under a special situation in Ref. 13 with a first-principle calculation. He studied the electronic properties of an adatom on a metallic surface, which could be regarded as an atomic chain with one atom connected to an electrode, and suggested that the Fermi energy of the adatom aligned itself to that of the metallic surface. The adatom was either filled or depleted with electrons, depending on the difference of the original work functions. The discussion in this article is consistent with this if the adatom is regarded as a shortest chain in Fig. 2(b).

Lang extended his calculation to an atomic chain with a few atoms[14] where Al atomic chains with one or three atoms showed larger conductance than that with two atoms. He assumed that the coupling of the chain atoms to the electrodes was so strong that the chain state densities were no longer discrete as in an isolated system, but had a significant width and overlap, showing only some peaks [corresponding to the situation between (2) and (3) in Sec. II]. Even in this case, there was a noticeable difference in transport properties between a two-atom chain, and one- and three-atom chains, and this article is consistent with his result. In fact, if the Al chain is isolated, the parallel p state along the Al chain is more modified than the perpendicular p states because the $V_{pp\sigma}$ coupling is stronger than the $V_{pp\pi}$ coupling as discussed in Ref. 5. The highest occupied molecular level is therefore due to this parallel p state and is not degenerate, so that the highest occupied level is partially filled in one- and three-atom chains whereas it is fully filled in a two-atom chain, which is the view here.

The prediction on the energy alignment in Fig. 2 may seem a simple repetition of an old theory for a junction of two macroscopic materials with different work functions.[6,7] It is pointed out that there would be a Fermi energy pinning

mechanism at the surface due to the surface states,[7] and that the energy discontinuity at the contact was not always a difference of two work functions. Such surface states do arise at the contact in our case, but only when the lattice constant of the chain is so short that the band crossing occurs, resulting in the Shockley surface states[4,15] (such a lattice constant is 4.2 Å for the Mg chain and 2.7 Å for the Si chain[3]). Except for this short lattice-constant limit, there is no intrinsic surface state. According to Ref. 7, surface contamination or the existence of foreign atoms on the surface would also bring about these surface states, but we usually have a contamination-free situation within atomic resolution under an ultrahigh vacuum STM environment. Thus, Fermi energy pinning by this contamination route is quite unlikely.

ACKNOWLEDGMENTS

The author is grateful to Professor Y. Yamamoto. Crucial discussions with Professor M. Heiblum on Coulomb interaction are greatly acknowledged.

[1]It is impossible to cover references on this topic systematically and satisfactorily. Some examples are: D. M. Eigler and E. K. Schweizer, Nature **344**, 524 (1990); J. A. Stroscio and D. M. Eigler, Science **254**, 1319 (1991); I.-W. Lyo and Ph. Avouris, *ibid.* **253**, 173 (1991); D. M. Eigler, C. P. Lutz, and W. E. Rudge, Nature **352**, 600 (1991); H. J. Hamin, S. Chiang, H. Birk, P. H. Guethner, and D. Ruger, J. Vac. Sci. Technol. B **9**, 1398 (1991); 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, Science **265**, 502 (1994).

[2]T. Yamada, Y. Takiguchi, D. Huang, and Y. Yamamoto, U.S. Patent, pending; D. Huang and Y. Yamamoto, Jpn. J. Appl. Phys. **135**, 3734 (1996).

[3]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).

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

[5]W. A. Harrison, *Electronic Structure and Properties of Solids* (Freeman, San Francisco, 1980); Surf. Sci. **299/300**, 298 (1994); Phys. Rev. B **24**, 5835 (1981); **31**, 2121 (1984).

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

[7]J. Bardeen, Phys. Rev. **71**, 717 (1947).

[8]S. Tomonaga, Prog. Theor. Phys. **5**, 544 (1950); J. M. Luttinger, J. Math. Phys. **4**, 1154 (1963).

[9]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.

[10]H. F. Chueng, Y. Gefen, E. K. Riedel, and W.-H. Shih, Phys. Rev. B **37**, 6050 (1988).

[11]Y. Imry, in *Directions in Condensed Matter Physics*, edited by G. Grinstein and G. Mazenko (World Scientific, Singapore, 1986), Vol. 1.

[12]Some examples of references are: 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, *ibid.* **72**, 2251 (1994); J. M. Krans, J. M. Van Ruitenbeek, V. V. Fisun, I. K. Yanson, and L. J. De Jongh, Nature **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).

[13]N. D. Lang, Phys. Rev. Lett. **56**, 1164 (1986).

[14]N. D. Lang, Phys. Rev. B **52**, 5335 (1995).

[15]W. Shockley, Phys. Rev. **56**, 317 (1939).