Photoelectron spectroscopy of atomic wires


aDepartment of Physics, UW-Madison, 1150 University Avenue, Madison, WI 53706, USA
bInstitut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany
cDonostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, San Sebastian, Spain

Abstract

Arrays of atomic wires can now be synthesized by self-assembly at stepped surfaces. They provide opportunities for exploring electrons in one dimension and to test predictions of exotic properties, such as spin charge separation in a Luttinger liquid.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photoemission; Fermi surface; One-dimensional; Quantum wire

1. One-dimensional electrons

One-dimensional physics is very elegant because of its mathematical simplicity [1,2]. Many problems can be solved analytically, and questions that are too difficult to address in higher dimensions become accessible. Electrons are predicted to exhibit exotic, if not paradoxical properties in one dimension, such as charge density waves, spin density waves, a Peierls gap, and spin charge separation. The high density of states that develops at one-dimensional Van Hove singularities is able to trigger a variety of instabilities, such as charge and spin density waves [3,4] and ferromagnetism [5]. Depending on various interaction parameters a rich phase diagram of exotic electron liquids develops, such as the Luttinger liquid [6–8] and the Luther-Emery liquid [9].

The Peierls theorem [10] implies that a one-dimensional metal might be a contradiction in terms. A half-filled, metallic band can lower its total energy by developing a mini-gap at the Fermi wave vector \( k_F \). Filled states move down in energy near the gap. Empty states move up, but do not count for the total energy. Since \( k_F \) coincides with the Brillouin zone boundary of a doubled unit cell for a one-dimensional band, such a gap opens naturally by pairing the atoms along a chain. There are loopholes in Peierls’ theorem that open the door to more exotic phenomena. For example, there can be several bands crossing the Fermi level and leading to \( k_F \) values that are different from those for period doubling [11]. Another way out is a rigid substrate that makes the cost in strain energy larger than the gain in electronic energy. Carbon nanotubes, for example, can be metallic given the correct chirality. Some one-dimensional chain structures of metal atoms at silicon surfaces exhibit metallic bands. They will be the main topic of this article.

If Peierls’ theorem can be overcome, the expected phenomena become quite exotic. In a Luttinger
liquid the electron loses its identity and separates into two quasiparticles, a spinon that carries spin without charge, and a holon that carries the positive charge of a hole without its spin [6–8]. These two quasiparticles have different group velocities and thus separate over time. Fig. 1 shows the energy versus momentum dispersion $\epsilon(q)$ of the two modes calculated for a one-dimensional Luttinger liquid [8]. The two branches exhibit nearly linear dispersions and cross each other at the Fermi level. The holon (light gray in Fig. 1) has about twice the group velocity $\frac{\text{d} \omega}{\text{d} k}$ compared to the spinon (dark gray), which leads to a rather counter-intuitive separation of spin and charge wave packets over time. The two branches overlap somewhat due to their finite width. The spinon peak still contains a small contribution from the tail of the holon peak, and vice versa. Therefore, it is possible to excite either one of them with a photon and eject a real photoelectron, including spin and charge.

The exotic behavior of electrons in a one-dimensional metal can be rationalized by a simple, classical picture. There are only two states at the Fermi level $E_F$, one with $k = k_F$, the other with $k = -k_F$. A classical electron may be viewed as a wave packet moving along a one-dimensional track. The wave packets corresponding to $k = \pm k_F$ move in opposite directions and completely overlap at some point, thereby generating maximum electron–electron interaction. In two and three dimensions such a situation is very improbable. The momenta of the electrons would have to be exactly opposite to each other. There is an infinite number of other $k$ points available on the Fermi surface. Due to the strong electron–electron interaction in one dimension there is no such thing as a single electron. Removing a single electron during the measurement starts a chain reaction that excites other electrons and leads to a collective excitation. Consequently, one may visualize a holon as a charge density wave and a spinon as spin density wave.

2. Fabricating atomic chains

Although a free-standing chain of atoms in vacuum sounds like a theorist’s fiction, it has actually been realized experimentally. Up to seven gold atoms may align themselves into a wire to bridge a small gap between two electrodes [12]. That is still a far stretch from an infinite chain. Therefore, the mainstay of one-dimensional condensed matter physics has relied on the traditional approach of using three-dimensional crystals consisting of weakly-coupled atomic or molecular chains. They produce a large measurement volume for bulk-sensi-

![Fig. 1. Spin-charge separation in a metallic Luttinger liquid, calculated from first principles. The energy versus momentum dispersion $\epsilon(q)$ of an electron splits into two sub-bands with different slope ($\sim$group velocity). The spinon band (dark gray) can be viewed as collective spin excitation, the holon band (light gray) as collective charge excitation. They intersect at the Fermi level $\epsilon=0$. From [8].](image-url)
tive experiments, such as neutron scattering. However, the residual coupling between the chains is difficult to control, and the experimentalist is left to the mercy of Nature’s quirks in forming crystalline structures. Polymers are more flexible and allow tailoring of the chain spacing by adding branches, but they do not order well. More recently, the synthesis of highly-perfect nanowires, such as carbon nanotubes, has stimulated the investigation of individual wires. The devices for probing the electronic structure on an individual nanowire are still rather rudimentary, however. It is very difficult to attach contacts to a single nanowire without getting it dirty or damaging it.

Several decades of experience in preparing ever more sophisticated surfaces have led to clean and well-ordered atomic chain structures at surfaces. That opens a new area of one-dimensional physics. Linking the chains to a crystalline substrate makes it possible to control their spacing with atomic precision. Metallic chains on a semiconducting substrate are less prone to undergo a Peierls transition because the rigid bonds to the substrate make the cost in strain energy too high. States at the Fermi level do not interact with the substrate because there are no states in the gap to interact with. Viewed this way, chains at a surface may actually be superior to a free-standing chain.

Stepped surfaces with a slight miscut from a crystallographic plane form ideal templates for atomic chains. The method of step decoration has turned out to be rather flexible, with at least two independent control parameters. The miscut angle determines the step spacing and thus the coupling between the chains. The metal coverage determines the number of atomic rows that are attached to the step edges, and thereby the number of independent wave functions forming conduction channels. Particularly interesting is the limit of a single atom per step. For varying the coupling along a chain one can change the size of the metal atom. Atoms with a magnetic moment will generate a magnetic coupling.

The most perfect step arrays have been fabricated at surfaces with a large-scale reconstruction, such as Si(111)7×7 [13,14]. In that case the formation of a kink (the native defect of a step array) requires adding many rows of atoms. That generates a kinetic barrier. For example, a kink at the Si(111)7×7 surface requires the addition of 14 atomic rows (7 rows two layers deep). Kink densities as low as one in 20,000 edge atoms have been achieved. With this scheme, the terrace width becomes quantized in unit cells of the reconstructed surface. The densest possible step array with a single unit cell as terrace produces a highly uniform step spacing [14].

Two chain structures induced on a semiconductor surface by metal atoms are shown in Fig. 2. One is formed by decorating steps on the vicinal Si(557) surface [15–18], the other forms on flat Si(111) by spontaneous symmetry breaking [18–22]. One of three possible 120° domains is stabilized on a surface with a small miscut of 1° that forces the chains to be parallel to the step edges. The STM images in Fig. 2 clearly demonstrate long chains with a small amount of extra atoms on top. These comprise about 0.02 monolayer for Si(111)–Au and 0.01 monolayer for Si(557)–Au. They are part of the equilibrium structure, but their role is not completely clear yet. They might act as dopants the ensure the optimum band filling. We will leave them out of the following discussion, arguing that they contribute a much smaller signal to the photoemission spectrum than the chains, which originate from 0.4 monolayer of Au for Si(111)–Au and from 0.2 monolayer of Au for Si(557)–Au.

The lattice period along the chain is doubled in some cases, possibly due to Si adatoms on every other lattice site. Adatoms tie up three broken bonds and trade them in for one. For clean Si(111)7×7 they provide the primary mechanism for lowering the surface energy. Adjacent chains seem to lack phase correlation since about half of the chains are arranged in a 2×2 zig-zag pattern, and the other half in a c(4×2) ladder structure. Such disorder leads to faint streaks at the half-order positions in diffraction experiments [23], as well as in the Fourier transform of the STM images. Uncorrelated chains have also been found for the honeycomb chain structure of Si(111)4×2–In [24].

3. Band mapping by photoemission

The most complete picture of the electronic structure of a solid is provided by angle-resolved photoemission [25]. It delivers the complete set of quan-
tum numbers for an electron in a solid, i.e., energy $E = \hbar \omega$, momentum $P = \hbar k$, spin, and point group symmetry. A pair of traditional, angle-resolved photoelectron spectra is given in Fig. 3, together with the $E(k)$ dispersion obtained from the peaks in a series of spectra. Recent detector developments have made it possible to simultaneously detect energy and angle and, thereby, acquire the $E(k)$ band dispersion in real time. An example is given in Fig. 4 for the two chain structures of gold on silicon whose STM images appeared in Fig. 2.

A second way of displaying the electronic states is in the form of constant energy surfaces, such as those shown in Figs. 5 and 6. For a two-dimensional surface state the Fermi surface is a one-dimensional curve. If the surface state is one-dimensional, this curve becomes a straight line perpendicular to the chains. The corresponding wave vector $k_y$ ceases being a quantum number and the energy surface cannot depend on it. Particularly important is the Fermi surface, which focuses on the part of the energy bands that is relevant to electronic phase transitions and transport properties [24,26–29]. All the relevant states are located within the thermally-accessible energy range of about $3.5 \, k_B T$ around the Fermi level ($k_B = $Boltzmann constant). For example, an electronic phase transition at a critical temperature $T_c$ rearranges the states near $E_F$ by opening an energy gap. The gap is $E_g \approx 3.5 k_B T_c$ at low temperature. (This holds in mean field theory, such as in the
Fig. 4. Band structure of stepped Si(557)–Au (left) versus flat Si(111)–Au (middle and right). Si(557)–Au produces a pair of half-filled, metallic bands (left). Si(111)–Au exhibits a single band shifted down by 0.3 eV (middle). The gap above that band is filled by additional, metallic bands in the second Brillouin zone (right). ZB corresponds to the zone boundary after doubling the chain periodicity. The \( E(k) \) band dispersion is acquired directly by \( E(k,q) \) multidetection. High photoemission intensity is shown dark. After [18].

Fig. 3. Photoelectron spectra for clean Si(111)\( 7 \times 7 \) and Au-covered Si(111). The peak positions at various emission angles are used to plot the \( E(k) \) band dispersion for the Au-induced \( 5 \times 2 \) chain structure. After [22].

BCS theory of superconductivity. The numerical factor 3.5 increases for strongly-coupled systems, such as high temperature superconductors, and reaches about 10 for a Peierls transition observed on the Si(111)\( 4 \times 1 \)–In surface [24].) Transport is dictated by the thermal width of the Fermi Dirac distribution. When using the full width half maximum of its derivative one obtains a numerical value of 3.5 \( k_B T \).

The two chain structures of Au on silicon in Fig. 2 both exhibit a unit cell that contains five atomic rows of the unreconstructed surface. On the Si(557)–Au surface there is an additional double-step in the unit cell. Although the two Si–Au structures have common features, some of the basic electronic characteristics are quite different, such as the Au content and the electron count. Si(557)–Au contains 0.2 monolayers of Au which is equivalent to a single Au row per unit cell. Si(111)\( 5 \times 2 \)–Au contains twice as much Au, i.e., 0.4 monolayers or the equivalent of two Au rows per unit cell. For determining the number of unpaired electrons per unit cell we start out with the unreconstructed Si(111)\( 5 \times 1 \) and Si(557) surfaces and add the Au atoms later. Extra silicon atoms incorporated during the reconstruction do not affect the parity of the electron count because they contain four electrons each. The unit cell of Si(111)\( 5 \times 1 \) contains 5 surface atoms with a single
broken bond each. Si(557)1×1 has 5 such atoms on the terrace, plus an extra atom with two broken bonds at the step edge, bringing the number up to 7. Next, we add Au atoms with an unpaired s-electron each. With 2 Au electrons for Si(111)5×1–Au and 1 Au electron for Si(557)–Au we obtain a total of 7 electrons for Si(111)5×1–Au and 8 electrons for Si(557)1×1–Au. In a naïve band model with two spin-paired electrons per band one would expect Si(111)–Au to be metallic and Si(557)–Au to be semiconducting. The experimental results are quite different from these expectations.

The band dispersions observed for the two Si–Au surfaces are shown in Fig. 4. Here we select the interesting region close the Fermi level and leave out a complicated set of lower-lying bands where the electrons with saturated bonds are located. Clear differences, such as a doublet of bands for Si(557)–
Au versus a singlet for Si(111)–Au, demonstrate that the electronic structure can be tailored by varying the step density and the Au coverage.

The Si(557)–Au bands extend all the way up to the Fermi level $E_F$ (Fig. 4 left). Therefore, this surface is metallic within the energy resolution of the experiment, which is limited to about 50 meV by inhomogeneous photovoltage broadening. The two closely-spaced bands cross $E_F$ close to the point of half filling (ZB in Fig. 4). One of them is slight less than half-filled, the other slightly more. Together they contain two electrons, which explains the even electron count (for a further discussion see Section 5).

The Si(111)–Au surface exhibits a single band with a dispersion similar to the two Si(557)–Au bands, but shifted down in energy by 0.3 eV (Fig. 4 middle). That gives the appearance of a semiconducting band structure. The resulting discrepancy with the odd electron count in a $5 \times 1$ unit cell is easily resolved by the observation of a doubled periodicity along the chains in STM images (Fig. 2). The extra Fourier component of the potential allows a gap to open up at the new zone boundary (ZB in Fig. 4). That is the same location as for a Peierls gap, but the magnitude of the gap is much larger. The STM images suggest that every other atom is missing along the observed chains, which creates a much larger disturbance than a small Peierls distortion.

For Si(111)–Au there exist additional, truly-metallic bands. They are barely visible in the 1st Brillouin zone (Fig. 4 middle), but dominate in the 2nd Brillouin zone (Fig. 4 right). One of the bands in the second zone appears to begin at $E_F - 0.3$ eV, where the band in the first zone disappeared. It fills the gap around the Fermi level and makes the surface metallic. Such a switch-over from one zone to the next has been observed in two- and three-dimensional bands. It is caused either by a different character of the wave functions or by a reversal of the group velocity at the zone boundary. A third possibility needs to be considered here as well. If the system has some two-dimensional character (see the next section), the bands in the 1st and 2nd one-dimensional zone are not equivalent. Overall, the spectra in Fig. 4 demonstrate that there is an elaborate fine structure in the bands near the Fermi level which has yet to be sorted out completely.

At both surfaces one finds sharp states near the Fermi level, where the lifetime broadening vanishes at low temperature (Figs. 3 and 4). Theory suggests that exotic phenomena might lurk in such one-di-
dimensional electron liquids. In the following, we will discuss two unusual electronic features found at these Si–Au surfaces that may be the beginning of more exotic phenomena to be discovered.

4. A band with variable dimensionality

The Si(111)5×2–Au surface exhibits a rather unusual band, which changes its dimensionality continuously from the top to the bottom. A look at its constant energy contours in Fig. 6 reveals a diagonal contour at the bottom which corresponds to a two-dimensional band dispersion in both $k_x$ and $k_y$; $(k_y$ is parallel to the chains). The tilt of the energy contour vanishes gradually towards the top of the band from panel (a) to (c). At the top, we have a one-dimensional contour that does not depend on $k_y$. The wave function of such a band must be quite unusual. At the top of the band it appears to be localized to a chain, at the bottom it extends out to neighboring chains. That is contrary to the expectation that states at higher energies are more delocalized. Furthermore, one might ask whether such a change in band topology is at odds with basic band theory.

In fact, a change in the dimensionality is quite compatible with band theory. As shown in Fig. 7, a simple tight binding model can be constructed that reproduces the band topology observed in Fig. 6. This is accomplished by a Hamiltonian that contains not only an intra-chain coupling $t_1$ and an inter-chain coupling $t_2$, but also a diagonal coupling $t_3$ [30]. Essentially, $t_2$ and $t_3$ are able to compensate each other at a particular line in $k_x$ space such that the dispersion perpendicular to the chains is eliminated. The tight binding bands with the three couplings $t_1$, $t_2$, $t_3$ in Fig. 7a are given by:

$$E(k_x,k_y) = E_0 + t_1 [\exp(ik_xa) + \exp(-ik_xa)] + t_2 [\exp(ik_yb) + \exp(-ik_yb)] + t_3 [\exp(i(k_xa + k_yb)) + \exp(i(k_xa - k_yb)) + \exp(i(-k_xa + k_yb)) + \exp(i(-k_xa - k_yb))]$$

where $E_0$ is a reference energy, and $a,b$, are lattice constants. The four parameters $E_0$, $t_1$, $t_2$, $t_3$ can be used to fit four points of the band structure, e.g., the corners of the surface Brillouin zone $\Gamma = (0,0)$, $X = (\pi/a,0)$, $Y = (0,\pi/b)$, $Z = (\pi/a,\pi/b)$

- $E_0 = (E_T + E_X + E_Y + E_Z)/4$
- $t_1 = (E_T - E_X + E_Y - E_Z)/8$
- $t_2 = (E_T - E_X - E_Y + E_Z)/8$
- $t_3 = (E_T - E_X - E_Y + E_Z)/16$

For obtaining the special case of a band with one-dimensional character along $XZ$ one demands $E_x = E_y$ and obtains the relation $t_1 = t_2/2$ between the perpendicular and diagonal coupling parameters. The resulting band dispersion is plotted in Fig. 7b. At the top of the band the dispersion vanishes, giving rise to a straight, one-dimensional energy contour along $k_x$ (dotted line) which resembles the experimental result in Fig. 6c. Farther down in energy the two-dimensional character develops continuously. The constant energy contours begin to tilt in the $k_y$ direction (compare the dotted lines in Fig. 7b with the experimental results in Fig. 6). The tight binding bands in Fig. 7 should be taken just as a model for the transition from one- to two-dimensional character. The actual Brillouin zone of Si(111)5×2–Au is only approximately rectangular and has different connectivity between 1st and 2nd zone [18,21]. The model in Fig. 7 is adjusted to simulate the bands in the smaller Brillouin zone of the doubled unit cell, i.e., after back-folding the band in Fig. 3 into the 1st zone at $ZB^{1/2}$.

The density of states in Fig. 7c exhibits a strong, one-dimensional singularity at the top of the band, which could give rise to one of the many instabilities that can occur in one-dimensional systems. The bottom of the band exhibits a two-dimensional step function as cutoff, and at the $\Gamma$ point one has a weak singularity from a two-dimensional saddle point.

5. The hunt for the Luttinger liquid

The Si(557)–Au surface provides another example of unusual behavior [16–18]. A closely-spaced pair
Fig. 7. Tight binding bands [30] varying continuously from one-dimensional at the top to two-dimensional at the bottom. Such a band topology can be achieved by compensating the coupling $t_z$ (perpendicular to the chains) with an extra, diagonal coupling $t_x$. (a) Couplings $t_{1}$, $t_{2}$, $t_{3}$ between neighbor atoms in real space. (b) Band dispersion in reciprocal space. The dotted lines correspond to the constant energy contours in Fig. 6. (c) Density of states, showing a strong one-dimensional singularity at the top of the band.

of bands with one-dimensional character is observed (Fig. 4 left). A previous study [16] suggested that this splitting represents spin-charge separation in a Luttinger liquid. Although our data in [17,18] are quite similar to the results in [16], the interpretation is not. There are two basic problems with an assignment of the two observed bands to the spinon and holon components of a single band, as in Fig. 1. The first hurdle is the even electron count (see Section 3). The spinon and holon components of a single band would contribute a single electron for both bands at half filling and lead to an odd electron count. The same argument can be made to rule out a spin splitting, even though such a splitting has been
observed for a Au(111) surface state [31]. A closer look at the predicted dispersion for the spinon and holon bands in Fig. 1 provides a second argument against spin-charge separation. Spinon and holon bands cross each other at $E_F$, while the bands in Fig. 4 left diverge slightly from each other when approaching $E_F$. Momentum distribution curves in [17,18] clearly demonstrate a finite splitting at $E = E_F$.

If this surface state is not a Luttinger liquid, what is the explanation of the closely-spaced pair of bands? A more conventional interpretation of the band splitting is based on two nearly-identical surface orbitals. Two orbitals in the unit cell generate bonding/antibonding combinations, which correspond to even/odd superpositions of the two wave functions. Such an assignment also explains the even electron count. Two normal, half-filled bands contribute one electron each. A possible structure with two nearly-equivalent orbitals would be a pair of silicon chains with half-filled broken bonds. Recent first principles calculations quantify this situation [32] and find a pair of closely-spaced bands at the Fermi level. A tempting candidate is the pair of atom chains that we observe by STM (see Fig. 2 and [17] for a close-up). However, they have a doubled period along the chain, which should produce a gap at the Fermi level analogous to the Peierls gap. An alternative would be a set of two orbitals located on a single chain, such as the $p_{3z}$ orbitals connecting the single Au row to the closest Si row in a zig-zag pattern. Investigations are under way to find the structure with the lowest total energy from first principles calculations and to determine its band structure [32,33]. Direct structural information from X-ray diffraction is becoming available [34]. Both come to the conclusion that the Au chain substitutes for a Si chain in the first layer. Surprisingly, this substitution happens in the middle of the terrace. Au does not decorate the step edge.

An interesting aspect of Si(557)–Au is its metallicity. The two bands in Fig. 4 left disperse straight through the Fermi level, without the complicated fine structure observed for Si(111)5×2–Au in Fig. 4 center and right. Such metallic behavior, combined with a fully one-dimensional band dispersion, demonstrates that Peierls’ theorem can be defeated. That opens the door for more exotic phenomena expected in one dimension.

6. Summary and outlook

A new group of one-dimensional materials is emerging that consist of atomic chains at surfaces. On the Si(111) surface, in particular, there is a class of chain structures induced by metal atoms at low coverage, such as Au, Ag, Gd, alkali metals and alkaline earths [18–22,35,36]. It is interesting to note that these low-coverage structures spontaneously break the three-fold symmetry of Si(111), while two-dimensional structures at higher coverage restore three-fold symmetry (e.g., $\sqrt{3}\times\sqrt{3}$). Vicinal Si(111) substrates stabilize one of the three possible domains and permit additional chain structures where a step is added to the unit cell.

It is encouraging to see that a metallic ground state can be obtained despite the tendency of a one-dimensional chain to double its period and become an insulator. Apparently, Peierls’ theorem can be bypassed by anchoring the chains to a rigid substrate such that the strain energy of a Peierls distortion becomes too large compared to the electronic energy gain from opening a band gap. A variety of unusual electronic features are observed that illustrate the potential for tailoring the electronic structure of one-dimensional chains and ladders at surfaces. Several parameters are available for steering a surface towards specific sections of the phase diagram of one-dimensional electrons, such as charge density waves, spin density waves, superconductivity, or exotic, non-Fermi liquids. The band filling can be varied by the metal coverage, the coupling between the chains by the step density, the coupling along the chain by the size of the adsorbed atoms. Even the spin structure might be controllable by using magnetic atoms, such as in recent work with Gd chains [36]. Although initial suggestions of spin-charge separation in such structures have not withstood closer scrutiny, there might be other chain structures that have the right combination of couplings for generating a Luttinger liquid. For designing one-dimensional surfaces it is highly desirable to have theoretical predictions of the parameter range re-
quired for spin charge separation, as well as for the parameter values that might be achievable with surface structures. With these in hand the photoemission spectra can be predicted using the one-step model (see [37] and Refs. therein).

Acknowledgements

FJH and AL would like to thank P.M. Echenique for the hospitality that enabled the collaboration on tight binding models. This work was supported by the NSF under Award Nos. DMR-9704196, DMR-9815416, and DMR-0079983. It is based upon research conducted at the Synchrotron Radiation Center, University of Wisconsin-Madison, which is supported by the NSF under Award No. DMR-0084402.

References