Fractional Band Filling in an Atomic Chain Structure

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A new chain structure of Au is found on stepped Si(111) which exhibits a 1/4-filled band and a pair of $\geq 1/2$-filled bands with a combined filling of 4/3. Band dispersions and Fermi surfaces for Si(553)-Au are obtained by photoemission and compared to that of Si(557)-Au. The dimensionality of both systems is determined using a tight binding fit. The fractional band filling makes it possible to preserve metallicity in the presence of strong correlations.

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One-dimensional physics is elegant because of its mathematical transparency. Many problems can be solved analytically, and questions that are too difficult to address in higher dimensions become accessible [1]. Electrons are predicted to exhibit exotic, if not paradoxical properties in one dimension [1–5], such as the separation of spin and charge in a one-dimensional metal. Even the concept of a single electron breaks down. Electrons cannot avoid each other when moving along one line, thus becoming excited collectively.

One might think that the ultimate one-dimensional metal would be a single string of atoms suspended freely in space. However, according to early arguments by Peierls, the atoms in such strings form pairs and open up a band gap. Recently, it has become possible to produce metallic chains of metal atoms that line up parallel to the step edges of vicinal silicon surfaces [5–12]. X-ray diffraction from the Si(557)-Au structure shows that gold atoms are incorporated rigidly into silicon lattice positions [12] without detectable Peierls distortion. While the Au atoms are locked to the Si substrate, the metallic electrons at the Fermi level are decoupled from the substrate because their energy lies in the band gap of Si.

Spin-charge separation has been suggested already [8] in Au chains on Si(557)-Au. Although this interpretation has been ruled out since [9], there is ample room for spin-charge separation to occur in other chain structures if the coupling parameters can be tuned [13]. The key parameter for metallicity is the band filling. Fractional filling is connected with exotic phases in a magnetic field, such as the fractional quantum Hall effect in two dimensions. One-dimensional organic compounds (Bechgaard salts) exhibit 1/4-filled bands that produce strongly correlated Mott states and charge density wave phases with spinon and soliton excitations [3,14–18].

The typical one-dimensional Tomonaga-Luttinger model starts with a 1/2-filled band containing one electron per unit cell, which then splits into a spinon and holon band. The energy scale of this many-electron effect can be boosted [13] by increasing the electron-electron interaction U. Signatures of spin-charge separation may be observable at energies comparable to the bandwidth W, as long as $U > W$. In this limit, however, a 1/2-filled band splits into a pair of insulating Hubbard bands and requires doping in order to retain its metallicity. The maximum carrier density is reached for a 1/2-filled Hubbard band, which evolves from a 1/4-filled normal band by increasing U.

We have found a chain structure of gold atoms on silicon, which exhibits a 1/4-filled band. Two additional bands somewhat above 1/2 filling bring the overall filling of the three metallic bands to exactly 4/3. Angle-resolved photoemission provides the Fermi surface [Figs. 1(a) and 1(b)], the band dispersion [Figs. 1(c) and 2(b)], and the intra- and interchain couplings t_1 and t_2. The 1/4-filled

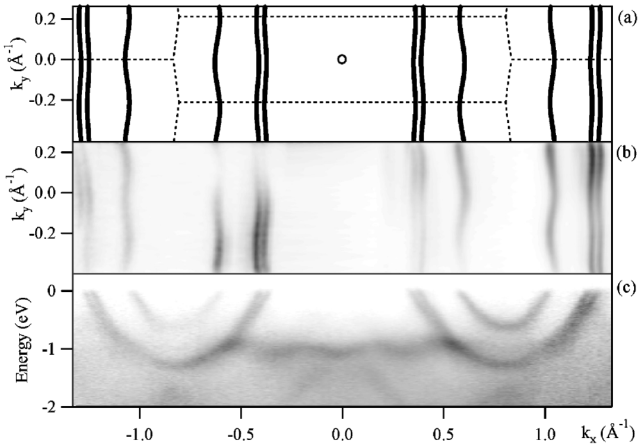

FIG. 1. Angle-resolved photoemission data of the band dispersion (c) and Fermi surface (b) of the Si(553)-Au chain structure. The Brillouin zone is given in (a), together with a tight binding fit to the Fermi surface. Three metallic bands disperse through the Fermi level ($E_F = 0$), two of them about 1/2 filled and one 1/4 filled. High photoemission intensity is shown dark. k_x is along the $[1\bar{1}0]$ chain direction and k_y along $[11\bar{2}]$.

band would be optimal for observing spin-charge separation if the electron-electron interaction U could be increased [13]. It turns out that U can be varied over a wide range for Si adatom states, from $U \approx 0.1$ eV on clean Si(111)(7×7) to $U = 2.0$ eV on hexagonal SiC(0001) [19]. A substantial $U = 0.8$ eV has been reported for chain structures as well [20], leading to a Mott insulator for Na atoms on top of Si(111)-(3×1)-Na.

Two chain structures of Au on stepped Si(111) are compared in Fig. 3. The new Si(553)-Au structure exhibits the 1/4-filled band. The Si(557)-Au surface lacks this band but has a similar band structure otherwise (Fig. 2). Si(553)-Au consists of Si(111) terraces $4\frac{1}{3}$ rows wide with a single broken bond at the step [Fig. 3(c)]. Si(557)-Au has two broken bonds at the step and a terrace width of $5\frac{2}{3}$ rows [Fig. 3(a)]. The corresponding miscut angles from Si(111) are 12.3° along the $[1\,1\,\bar{2}]$ azimuth for (553) and 9.5° along $[\bar{1}\,\bar{1}\,2]$ for (557). Scanning tunneling microscopy (STM) shows a 1×1 unit cell with 1×3 vacancy defects for Si(553)-Au [Fig. 3(d)], and a 1×2 reconstruction with adatom defects for Si(557)-Au [Fig. 3(b)]. Both contain a single gold chain per unit cell. We have performed first principles, total energy calculations for > 40 structural models of Si(553)-Au. These indicate that gold substitutes Si surface atoms in the center row of the terrace [Fig. 3(c)]. The local bond geometry is similar to that obtained for Si(557)-Au from total energy calculations [11,21] and x-ray diffraction [12]. The Si atoms near the steps rearrange themselves into honeycomb chains (not shown in Fig. 3, see [21,22]).

The gold chain structures were characterized at room temperature by STM and low energy electron diffraction (LEED), until they could be reproduced accurately in the angle-resolved photoemission setup at the Synchrotron Radiation Center (SRC). LEED was available in both locations and was used to ensure that the surface structures were identical. The most critical part was the Au coverage (0.24 ± 0.04 monolayers for Si(553)-Au and 0.2 for Si(557)-Au [8,9]). Photoemission features became broader when departing from the optimum coverage, but the band filling did not change. The Au evaporator was calibrated by preparing pure Si(111)5×2 without 7×7 or $\sqrt{3} \times \sqrt{3}$-Au admixtures [9,10]. During deposition the substrate was held at 650 °C with a post-anneal at 830 °C. Photoemission data were acquired at 160–220 K using a hemispherical Scienta SES200 spectrometer with simultaneous angle and energy multidetection ($h\nu = 34$ eV, p polarization along k_x). A photovoltage shift of the Fermi level needed to be taken into account at low temperature.

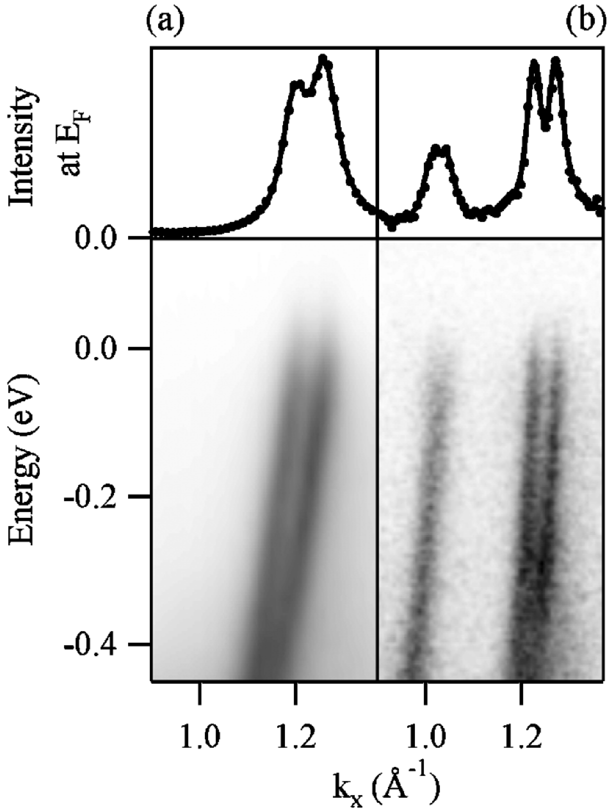

FIG. 2. Expanded $E(\mathbf{k})$ photoemission data of the Fermi level crossings for (a) Si(557)-Au and (b) Si(553)-Au. Both exhibit a doublet of 1/2-filled bands, and Si(553)-Au an extra 1/4-filled band.

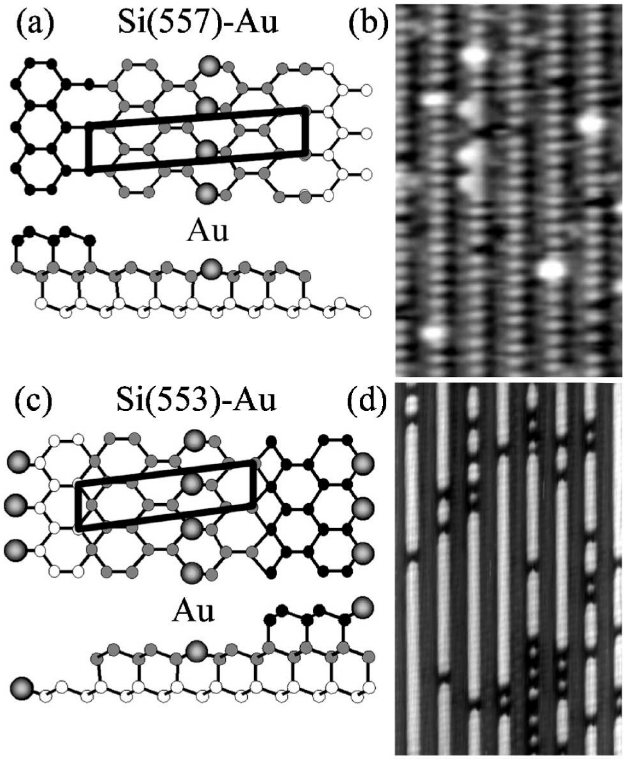

FIG. 3. Comparison between the Si(557)-Au and Si(553)-Au chain structures (top and bottom). Both contain a single Au chain replacing the Si row at the center of the terrace. The rearrangement of Si atoms has been omitted. The STM images on the right exhibit 1×2 periodicity for Si(557)-Au and 1×1 for Si(553)-Au with 1×3 defects. 12×20 nm^2.

The $E(k_x)$ band dispersion in Fig. 1(c) contains three metallic bands, all with their minima at the Brillouin zone boundary of the 1×1 unit cell. A closely spaced pair of 1/2-filled bands crosses E_F at $k_F = 0.36\ \text{Å}^{-1}$ and $0.40\ \text{Å}^{-1}$, about half way to the Brillouin zone boundary at $\pi/a = 0.82\ \text{Å}^{-1}$. It resembles the doublet observed on Si(557)-Au (Fig. 2). In addition, Si(553)-Au exhibits a band with 1/4 filling and $k_F = 0.60\ \text{Å}^{-1}$. The Fermi surface in Fig. 1(b) exhibits weak two-dimensional undulations around the straight lines that a purely one-dimensional Fermi surface would give. The $E(k_x)$ band dispersion in Fig. 1(c) is taken at the "neutral" point ($k_y = 0.11\ \text{Å}^{-1}$) where the undulation passes through zero. The Fermi level crossings are very sharp, as shown in a closeup in Fig. 2(b) (top). Their full width half maximum is $\delta k_x = 0.03\ \text{Å}^{-1}$, one of the sharpest observed for any semiconductor surface and sharper than for Si(557)-Au (Fig. 2 top). The inverse width $l = \delta k_x^{-1}$ gives a coherence length of at least nine atom spacings, given the limited momentum resolution of the spectrometer. The chains in Fig. 3(c) have an average length of nine atoms with a significant number of undisturbed chains reaching 30 atoms. Recently, the Si(557)-Au chain structure has been reported to be the most perfect chain structure because it exhibits the sharpest Fermi cutoff ever observed in 1D systems [23]. We find that the Fermi cutoff is actually sharper for Si(553)-Au than Si(557)-Au.

In order to obtain accurate filling numbers we integrate over the occupied part of **k** space enclosed by the three Fermi surfaces and normalize to two electrons per band over the full Brillouin zone. According to Luttinger's theorem [24] this simple box quantization method continues to be valid for an interacting electron system as long as perturbation theory is valid. It would break down for a Mott transition to an insulator, however. After careful integration over the full Fermi surface we find all three bands to be filled somewhat above their exact fractions of 1/2 or 1/4 (Table I, first column). Combined, however, they produce a filling of 1.338 which coincides with the fraction 4/3 within our accuracy of ±0.015.

To quantify the one- and two-dimensional couplings we have used a tight binding model with one-dimensional couplings t_1 and t_3 to nearest and second nearest neighbors along the chain and a two-dimensional coupling t_2 between chains. Such a parametrization can be used in a many-electron Hamiltonian [19]. The band dispersion and the Fermi surface are given by the following:

(i) $E(k_x, k_y) = E_0 + t_1[\exp(ik_xa) + \exp(-ik_xa)] + t_3[\exp(ik_x2a) + \exp(-ik_x2a)] + \frac{1}{2}t_2\{\exp[i(k_xa/2 + k_yb)] + \exp[i(k_xa/2 - k_yb)] + \exp[i(-k_xa/2 + k_yb)] + \exp[i(-k_xa/2 - k_yb)]\} = E_0 + 2[t_1\cos(k_xa) + t_3\cos(2k_xa) + t_2\cos(k_xa/2)\cos(k_yb)]$,

(ii) $k_y(k_x) = b^{-1}\arccos\{[\frac{1}{2}(E_F - E_0) - t_1\cos(k_xa) - t_3\cos(2k_xa)]/t_2\cos(k_xa/2)\}$.

Note that there are four closest neighbors in adjacent chains, separated by $\pm a/2$ in x and by $\pm b$ in y [$a = 3.84$ Å, $b = 14.8$ Å for Si(553), $b = 19.1$ Å for Si(557)]. First the couplings t_1 and t_3 are determined from the band dispersion in Fig. 1(c) along the neutral direction $k_y = \pi/2b$ where t_2 does not contribute. Then, t_2 is determined by matching the oscillations of the Fermi surface. The resulting calculated Fermi surface [Fig. 1(a)] and $E(k_y)$ dispersion (not shown) are in excellent agreement with experiment. The resulting values of the band parameters are listed in Table I. For Si(553)-Au, the two 1/2-filled bands are more one dimensional than the 1/4-filled band, with a ratio $t_1/t_2 = 46, 39$ versus 12. And the doublet of Si(557)-Au is even more one dimensional with $t_1/t_2 > 70$. The increase in chain spacing from 14.8 to 19.1 Å reduces the two-dimensional coupling below the detection limit.

One can compare our results with other one-dimensional systems that exhibit fractional band filling, such as organic Bechgaard salts [2,14,15] with 1/4 filling. Their intrachain coupling $t_1 \approx 0.3$ eV is significantly smaller than that of Au chains on silicon ($t_1 = 0.6$–1.0 eV). The coupling ratio $t_1/t_2 \approx 10$ in Bechgaard salts is exceeded by that for Au chains (t_1/t_2 from 10 to > 70), indicating stronger one-dimensional character for atom chains at surfaces. Furthermore, the three-dimensional coupling is completely absent for metallic states in the gap of silicon, but finite in Bechgaard salts (≈ 1 meV).

There is an intriguing (although by no means settled) explanation for the fractional band filling of 4/3 and the resulting electron count of 8/3 per 1×1 unit cell, again a fractional number. A 1×3 unit cell containing two extra Si atoms contains eight extra valence electrons, i.e., 8/3 electrons when distributed over three cells of the 1×1 chain. The 1×3 structure of the defects in Fig. 3(d) demonstrates the existence of such a unit cell.

TABLE I. Band parameters (see text) for Au chains on stepped Si(111). The bandwidth is $W_x = 4t_1$ along k_x and $W_y = 4t_2$ along k_y. The bottom of the band is $E_{\min} = E_0 - 2t_1 + 2t_3$. The effective masses range from 0.3 to 0.65.

	Filling	E_0 [eV]	t_1 [eV]	t_3 [eV]	t_2 [eV]	v_F [10^6 m/s]
Si(553)-Au	0.272	1.28	0.96	<0.03	0.08	0.9
	0.509	0.04	0.73	0.065	0.016	1.0
	0.5 − 0.1657	−0.16	0.63	0.065	0.016	1.0
Si(557)-Au	0.46	0.35	0.77	0.10	<0.01	1.0
	0.54	0.01	0.61	0.10	<0.01	1.0

The remainder of the chain structure might have a 1 × 3 symmetry that fluctuates on the time scale of a STM scan ($\approx 10^{-2}$ s/atom), analogous to the vibrating 2 × 1 dimers on Si(100) which are pinned into a larger $c(4 \times 2)$ unit cell at defects. Photoemission operates on a much shorter time scale ($\approx 10^{-15}$ s) and can take a snapshot of these fluctuations. Indeed, there is a filled band in Fig. 1(c) near -1 eV with a 1 × 3 (or 1 × 6) periodicity. There is no evidence of a 1 × 3 period for the metallic bands at E_F. Apparently, the one-dimensional chain states are not perturbed by the two-dimensional 1 × 3 cell where they are embedded. A similar situation exists for Si(557)-Au, where a 1 × 2 reconstruction is observed by STM but not in the dispersion of the metallic bands. Our model of autodoping a one-dimensional chain by a two-dimensional reservoir surrounding it has a well-known analog: It is a low-dimensional version of the doping mechanism in high temperature superconductors, where the two-dimensional CuO plane is doped by atoms in the three-dimensional unit cell embedding it.

In summary, we have found a chain structure of Au atoms on stepped silicon that exhibits a band near 1/4 filling, together with a fractional electron count of 8/3 electrons per 1 × 1 cell. A possible (but not unique) explanation is suggested where two extra Si atoms in a 1 × 3 cell "dope" the 1 × 1 cell of the gold chain with 8/3 electrons. A quarter-filled band makes it possible to increase electron correlations without losing metallicity due to a Mott-Hubbard transition. That creates an opportunity for observing large spin-charge separation effects [13]. As a next step one could explore chain structures on substrates with larger on-site electron-electron coupling U, for example, on hexagonal SiC(0001), where values of U as large 2 eV have been reported [19]. In fact, long chains of Si dimer orbitals have been observed on cubic SiC(100) already [25]. The possibility of arranging atomic chains by STM [26] provides extra flexibility.

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[1] *Mathematical Physics in One Dimension*, edited by Elliott H. Lieb (Academic Press, New York, 1966); *Physics in One Dimension*, edited by J. Bernasconi and T. Schneider (Springer, Berlin, 1981).

[2] V. Meden and K. Schönhammer, Phys. Rev. B **46**, 15 753 (1992).

[3] P. M. Chaikin, E. I. Chasheschkina, I. J. Lee, and M. J. Naughton, J. Phys. Condens. Matter **10**, 11 301 (1998); D. G. Clarke, S. P. Strong, P. M. Chaikin, and E. I. Chashechkina, Science **279**, 2071 (1998).

[4] M. Grioni, I. Vobornik, F. Zwick, and G. Margaritondo, J. Electron Spectrosc. Relat. Phenom. **100**, 313 (1999).

[5] F. J. Himpsel, K. N. Altmann, R. Bennewitz, J. N. Crain, A. Kirakosian, J.-L. Lin, and J. L. McChesney, J. Phys. Condens. Matter **13**, 11 097 (2001).

[6] H.W. Yeom, S. Takeda, E. Rotenberg, I. Matsuda, K. Horikoshi, J. Schäfer, C. M. Lee, S. D. Kevan, T. Ohta, T. Nagao, and S. Hasegawa, Phys. Rev. Lett. **82**, 4898 (1999).

[7] M. Jalochowski, M. Strozak, and R. Zdyb, Surf. Sci. **375**, 203 (1997).

[8] P. Segovia, D. Purdie, M. Hengsberger, and Y. Baer, Nature (London) **402**, 504 (1999).

[9] R. Losio, K. N. Altmann, A. Kirakosian, J.-L. Lin, D. Y. Petrovykh, and F. J. Himpsel, Phys. Rev. Lett. **86**, 4632 (2001).

[10] K. N. Altmann, J. N. Crain, A. Kirakosian, J.-L. Lin, D. Y. Petrovykh, F. J. Himpsel, and R. Losio, Phys. Rev. B **64**, 035406 (2001).

[11] D. Sánchez-Portal, J. D. Gale, A. García, and R. M. Martin, Phys. Rev. B **65**, 081401 (2002).

[12] I. K. Robinson, P. A. Bennett, and F. J. Himpsel, Phys. Rev. Lett. **88**, 096104 (2002).

[13] R. Claessen, M. Sing, U. Schwingenschlögl, P. Blaha, M. Dressel, and C.S. Jacobsen, Phys. Rev. Lett. **88**, 096402 (2002).

[14] V. Vescoli, F. Zwick, W. Henderson, L. Degiorgi, M. Grioni, G. Gruner, and L. K. Montgomery, Eur. Phys. J. B **13**, 503 (2000).

[15] D. Poilblanc, G. Montambaux, M. Héritier, and P. Lederer, Phys. Rev. Lett. **58**, 270 (1987).

[16] S. Biermann, A. Georges, T. Giamarchi, and A. Lichtenstein, cond-mat/0201542.

[17] F. H. L. Essler and A. M. Tsvelik, Phys. Rev. Lett. **88**, 096403 (2002).

[18] F. Mila and K. Penc, Phys. Rev. B **51**, 1997 (1995); K. Penc and F. Mila, Phys. Rev. B **50**, 11 429 (1994).

[19] F. Flores, J. Ortega, and R. Perez, Surf. Rev. Lett. **6**, 411 (1999); R. Losio, K. N. Altmann, and F. J. Himpsel, Phys. Rev. B **61**, 10 845 (2000); L. I. Johansson, F. Owman, and P. Martensson, Surf. Sci. **360**, L478 (1996); J.-M. Themlin, I. Forbeaux, V. Langlais, H. Belkhir and J.-M. Debever, Europhys. Lett. **39**, 61 (1997); V. Ramachandran and R. M. Feenstra, Phys. Rev. Lett. **82**, 1000 (1999).

[20] J. R. Ahn, N. D. Kim, S. S. Lee, K. D. Lee, B. D. Yu, D. Jeon, K. Kong, and J.W. Chung, Europhys. Lett. **57**, 859 (2002).

[21] S. C. Erwin *et al.* (to be published).

[22] S. C. Erwin and H. H. Weitering, Phys. Rev. Lett. **81**, 2296 (1998).

[23] P. Starowicz, O. Gallus, Th. Pillo, and Y. Baer, Phys. Rev. Lett. **89**, 256402 (2002).

[24] K. B. Blagoev and K. S. Bedell, Phys. Rev. Lett. **79**, 1106 (1997).

[25] P. Soukiassian, F. Semond, A. Mayne, and G. Dujardin, Phys. Rev. Lett. **79**, 2498 (1997).

[26] N. Nilius, T. M. Wallis, and W. Ho, Science **297**, 1853 (2002).