

One-dimensional nanostructures on semiconductor surfaces – structures and electronic bands

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I. Introduction

Basic terminology for semiconductor surfaces - Because of the lack of translational symmetry on the 'surface', surface atoms form quasi two dimensional (2D) structures of their own, which are distinguished from those of 'bulk'. These quasi 2D systems, thus, have provided a variety of interesting physical phenomena, which cannot be encountered in bulk.¹⁻³ Furthermore, understanding of these surface phenomena has great importance in modern high-technology, for typical examples, the growth and process of electronic device materials and the catalysis in chemical engineering. It can be said that surface physics and chemistry starts from investigating the ground state properties, the geometric and electronic structures, of a given surface.¹⁻³

An 'ideal surface', which is formed by truncation of a bulk crystal, for example, of a covalent semiconductor with sp^3 hybridization, is left with numerous broken bonds of high free energy. The surface atoms try to rearrange themselves to reach a lower energy configuration. This rearrangement is called the 'surface reconstruction' such as the 2×1 or $c(4 \times 2)$ structure on Si(001) (see below for details) and the 7×7 structure on Si(111).⁴ If extrinsic atoms, 'adsorbates', are put on a clean surface with a certain surface reconstruction, then the geometry of surface atoms can change further through bondings with adsorbates. These 'adsorbate-induced reconstructions' of surface atoms provide more varieties in surface structures and a wide variety of new 2D materials systems.⁴

On the other hand, surface reconstructions cause electronic structures specific to the surface layers. For instance, the broken bonds of surface atoms of ideal semiconductor surfaces, called 'dangling bonds (DB)', will cause new electronic states in the bulk band gap.¹⁻³ These dangling bond orbitals are basically well-localized. However, if there is periodic array of them and finite overlap between neighboring DBs, then they may form 2D electronic bands, the 'surface-state bands'.⁵ Since the wave functions for a surface state are localized in the surface layer and decays exponentially into the bulk, a surface state band has no well defined Bloch wave vector k along the surface normal, in other words, no dispersion along the surface normal.¹⁻³

As easily expected, the surface reconstructions of clean surfaces and by adsorption will create different kinds of surface electronic orbitals, bonding or antibonding orbitals, which originate from the bonds (or interaction in general) between adsorbates and substrate atoms, between substrate surface atoms and between adsorbates themselves. These bonding or antibonding orbitals may also form 2D surface-state bands of their own.^{1,5}

Simple examples; dimer row reconstructions on Si(001) - A nice and simple example of surface reconstructions and surface states are the dimer reconstructions on the Si(001) surface.^{5,6} The ideal clean Si(001) surface has surface atoms with two DBs each. The surface Si atoms then reconstruct by forming bonding with neighboring atoms with these DBs. This results in formation of symmetric dimers (dimer rows) in a 2×1 periodicity. The two DBs left on each dimer further interact to form a π -bond. The electronic states (orbitals) localized on a Si symmetric dimer are then, four 'back-bonds', one 'dimer-bond' and one 'DB π -bond'.⁵ However, the π -bonding is in fact inherently unstable against the fluctuation (transfer) of charge or the buckling of dimers and the stable structure of the Si(001) surface is antiferromagnetically buckled

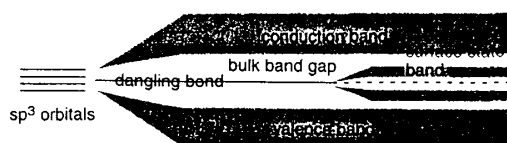


Fig. 1 Schematics of surface reconstruction and surface-state band formation.

asymmetric dimers (a $c(4 \times 2)$ periodicity).^{7,8} (Ideal symmetric dimers with DB π -bonds can be found on the Diamond(001) surface.)⁸ Within the asymmetric dimers the DB electrons are localized on one of the dimer atoms buckled-upwards, which is called 'up-dimer-atom state' and is observed with characteristic dispersions in photoemission.^{5,8} This dimer structure is a really fundamental and general aspects for the surface reconstructions of the (001) surfaces of most of the elemental and compound semiconductors and also for the adsorption on those surfaces.⁵

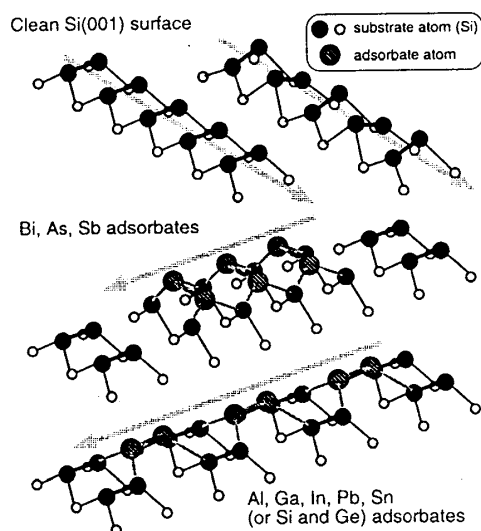


Fig. 2a Dimer structures on Si(001).

If there are group-V element adsorbates on Si(001), the adsorbates form symmetric dimers of their own and break the substrate Si dimers. Then we will have four back-bonds, one dimer-bond and two 'lone pair orbitals' on each adsorbate dimer. These characteristic lone-pair-orbitals are also observed as a dispersing surface state within the band gap.⁵ For the group-V dimers, the dimers are perpendicular to the substrate dimers and these dimer rows form 1×2 structure at 1 ML coverage (called 'perpendicular symmetric dimers'). For the case of group-III metal adsorption, a completely different dimer structure is formed; a 2×2 phase is formed at 0.5 ML with adsorbates dimers on 'unbroken' Si dimers and with the dimer orientation parallel to Si dimers (called 'parallel symmetric dimers').⁹ A group-III dimer has only four back-bonds and one dimer-bond. The surface-state bands from all of them have been observed (discussed in detail

below).¹⁰

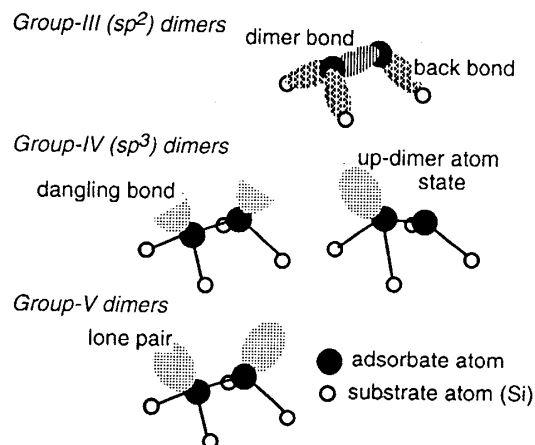


Fig. 2b Electronic orbitals of dimer structures on Si(001.)

The parallel symmetric dimers have been found also for the group-IV adsorbates of Pb and Sn on Si(001).¹¹ It has been thought that the adsorption of other group-IV elements of Ge and Si results in perpendicular dimer structures of asymmetric dimers. However, this is true only for Si adsorption at 1 ML. For Ge adsorption the mixed Ge-Si dimers in perpendicular asymmetric configuration were observed.¹² Moreover, the low-coverage, low-temperature Ge or Si adsorption results in various metastable configurations of both parallel symmetric dimers, perpendicular asymmetric dimers and more, which are crucial in understanding the epitaxial growth on Si(001).¹³

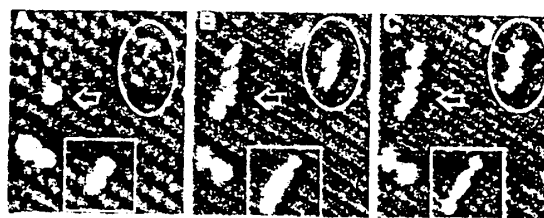


Fig. 3 Ge adsorption on Si(001) (STM images).¹³

Motivation for 1D nanostructures on surfaces ; Exotic and new 1D metals ? - As mentioned above, the new materials systems due to surface reconstructions and adsorbates have provided many new interesting fields of condensed matter physics. One of recent interests are the 1D nanostructures (or quantum wires) formed on solid surfaces. The 1D solids, periodic arrangements of atoms and molecules

in strongly anisotropic or linear patterns, (especially 1D metallic systems) feature exotic and attractive physical phenomena such as the instability of a metallic phase (Peierls instability), anomalous phonon dispersion (Kohn anomaly), spin or charge density wave, triplet superconductivity and non-Fermi-liquid behavior.¹⁴ The most well-known example is Peierls instability, where the electrons and holes near the Fermi level couple with a static lattice vibration leading to a spatial modulation of charges [charge density waves (CDW)] and to opening an electronic energy gap at Fermi level. So far, only very limited number of materials have been shown to have 1D electronic properties such as a few organic conductors, Pt chain compounds ($\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 3.2\text{H}_2\text{O}$), transition metal chalcogenides (NbSe_3) and transition metal bronzes ($\text{K}_{0.3}\text{MoO}_3$).¹⁴

Surface systems are good candidates to find new 1D materials due to their inherent low dimensionality and due even to the possibility of atom manipulations. Furthermore, in contrast to the known 1D materials, the surface 1D systems, if any, have no 3D coupling between the 1D chains, which may yield new physical properties. Not only elucidating the exotic 1D physical properties, but the study of quantum wires on semiconductor surfaces will provide important building blocks for the future nanometer-scale electronic and magnetic device technology.

Several examples of 1D nanostructures on metal and semiconductor surfaces - In recent years, indeed many nanoscale 1D chain structures have been observed on various surfaces mostly through the scanning tunneling microscopy (STM) investigations. On metal surfaces, the famous examples extend from (1) regular arrays of steps and adsorbates preferentially

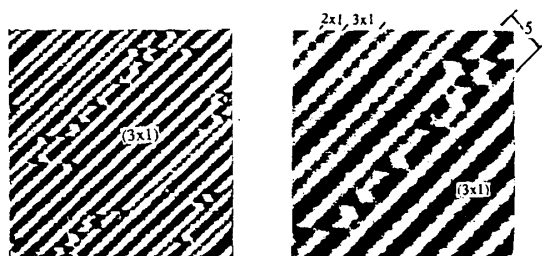


Fig. 4 1D 'psuedomolecules' on Ag(110) (STM images).¹⁶

adsorbing on step edges ($\text{Ni}(7,9,11)$),¹⁵ (2) 1D

polymer-like reaction products with O_2 (H_2) reaction on Cu(110) and Ag(110) ($\text{Ni}(110)$) surfaces¹⁶ and (3) domain boundaries on disordered alloy (FeSi) surfaces¹⁷ to (4) ordered surface alloy of Au/Cu(001).¹⁸

On semiconductor surfaces, a variety of 1D chains can be discussed such as (1) missing dimer chains on the Ge/Si(001)¹⁹ and Bi/Si(001) surfaces,²⁰ (2) Bi embedded wires on Si(001),²¹ (3) Al, In,²² Ga, Pb,¹¹ Sn dimer chains on Si(001), (4) Si dimer wires on SiC(001),²³ (5) diamond-like C wires on SiC(001),²⁴ (6) Ga wires on H-terminated Si(001),²⁵ (7) In and Au chains on Si(111) (ref. 26) and (8) C_2H_4 molecular chains on Si(001).²⁷ The following parts of this lecture will concentrate on several such 1D quantum wires on semiconductor surfaces.

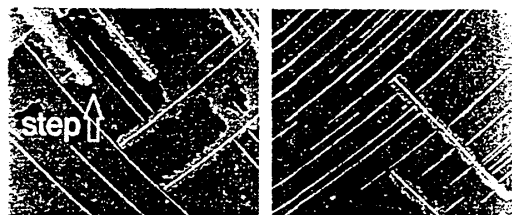


Fig. 5 Bi-Si quantum wires on Si(001) (STM images).²¹

II. Methods of investigation ; Photoelectron spectroscopy for solid surfaces

Overview of PES - The ways of approaching the 1D quantum wires on surfaces can be multifold; (1) investigating the ground state structures – atomic structures, chemical bondings and electronic band structures, (2) investigating the kinetics and dynamics to understand the mechanism of formation and (3) investigating the transport, magnetic and optical properties. In this lecture, mostly the first approach, especially for the chemical bondings and electronic band structures, will be discussed. The most powerful and direct experimental way of investigating the chemical bondings and electronic band structures is photoelectron spectroscopy (PES).²⁸

In PES techniques, basically the energy, momentum and spin of photoelectrons, the electrons ejected from the near surface layers by absorbing the kinetic energy of irradiated photons, are analyzed to determine the binding energy, Bloch wave vector and spin state of the initial electronic states. Due to the short mean free path of photoelectrons within the

matter (5 – 100 Å), this technique is inherently surface sensitive. Several different kinds of surface-related information can be obtained in PES.

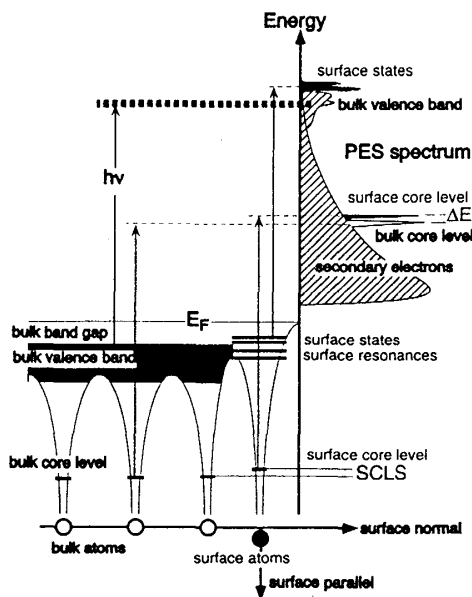


Fig. 6 Overview of photoelectron spectroscopy.

ARPES and Fermi surface mapping - At first, angle-resolved measurements of photoelectrons from valence bands, called angle-resolved photoelectron spectroscopy (ARPES), allow the determination of 2D band structures of surface states since the 2D in-plane electron momentum is conserved through the photoemission process. This is far more clear for the semiconductor surface states well inside the bulk band gap.²⁹ Especially for the low-dimensional metallic systems, the detailed shape of Fermi surfaces are of prime importance for their physical properties, which can be determined by ARPES.³⁰ The most convenient and successful way of measuring Fermi surfaces (contours) is the so-called 2D angle-scan PES; angle-resolved photoelectron intensities from the small energy window centered at Fermi level are measured as a function of the 2D electron wave vector (emission angles).

Surface core levels and PED - At second, the measurements of core levels with sufficient energy resolution can resolve out the 'surface core levels' of surface layers, that is the energy-shifted core levels of surface atoms from those of bulk atoms. The core levels of adsorbates can be investigated to find different core level binding energies due to different

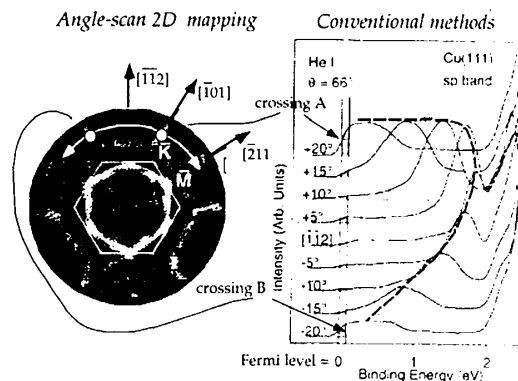


Fig. 7 Fermi surface mapping through 2D angle-scan PES.

kinds of chemical and structural environments of adsorbates.³¹ These surface core levels or surface core level shifts can now be calculated by *ab initio* methods and bring important qualitative chemical, structural and sometimes dynamical information.

The angular (or energy) distribution of photoelectron intensities from a core level can be measured, which reflects the surface structures through the scatterings of photoelectrons from an atom with surrounding atoms and the consequent interferences between the scattered and directly-emitted photoelectron waves (the phenomenon called photoelectron diffraction (PED)).³² Detailed analyses of these angular or energy distributions, called angle-scan or energy-scan PED patterns, can lead one to quantitatively determine the surface structures.

Together with the complementary surface techniques of LEED, RHEED and STM, we have a quantitative structural, chemical and electronic probe for a given surface system by PES.

III. Recent examples of 1D nanostructures on semiconductor surfaces

Covalently bonded In (Al) chains on Si(001) and surface polymerization - As mentioned above, In, Al, Ga, Pb, and Sn adsorbates form 1D parallel symmetric dimer chains, which develop into a well ordered 2x2 phase at 0.5 ML.^{9-11, 22} These quantum wires (sometimes extends to a length of several 100 Å) attracted much recent attention as candidates for observing interesting 1D physical properties.³³

Since the key for the understanding of the possible 1D properties lies on the behavior of electrons, the electronic band structures of In, Al, Ga and Pb-induced

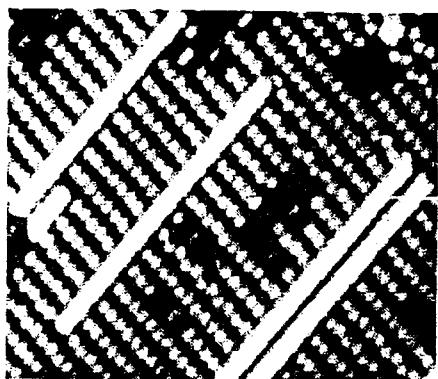


Fig. 8 In quantum chains on Si(001) (STM images).²²

2x2 surfaces have been studied extensively.¹⁰ For example, Fig. 9 shows the surface -state band dispersions measured for the 2x2-In and -Al surfaces by ARPES. These series of studies all consistently showed that (1) the quantum wire phases are semiconducting with a rather large band gap (~ 1 eV), (2) there are five surface-state bands within the bulk band gap and (3) the surface band structures of 2x2-In, Ga, and Al (and even probably Pb) are essentially the same. Through detailed investigation of these surface state bands and through comparison to *ab initio* density-of-states calculations, it was clearly concluded that these five surface states correspond to the four back bonds and one dimer bond of an adsorbate dimer.

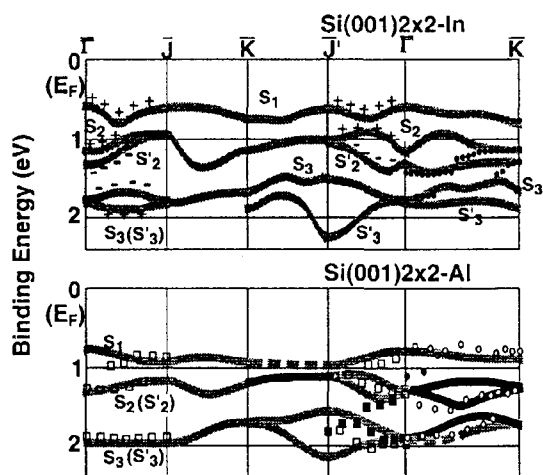


Fig. 9 Experimental dispersions of the surface state bands for the 2x2-In and -Al surfaces.

Although a STM study on In quantum wires has suggested Peierls pairing as the mechanism of the dimer formation, the experimental and theoretical electronic

structure studies consistently indicate that the dimers are covalently bonded with well-localized surface electrons.³³ The ARPES results for the surface-state bands also show that there is no 1D anisotropy in the band structure of the quantum wires in clear contrast to their 1D appearance in STM and to the strong anisotropy in initial growth. *That is, electronically these quantum wires are not a 1D materials system.* The STM images were in this respect a lot misleading and the initial anisotropic growth (or the quantum wire formation) was successfully explained by 'surface polymerization', where only the local bondings of adsorbates and substrates are important instead of 1D electronic coupling.³⁴

Zero dimensional Si chains on SiC(001) and cellular fluctuation - One of the most recent example of 1D quantum wire studies is the highly-stable and highly-controllable quantum chains of Si atoms on the 3C-SiC(001).²³ The atomic scale 'wires' shown in the STM (Fig. 10a)³⁵ are composed of Si dimers.³⁶ The density of these 'quantum' wires, whose length is as long as $\sim 1 \mu\text{m}$, can be controlled quite easily and the most dense phase of them is the 3x2 phase.

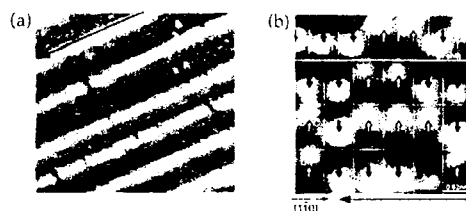


Fig. 10 (a) Si quantum wires on 3C-SiC(001) (STM image) and (b) an empty state STM image of the 3x2 phase composed of the quantum wires.³⁵

The band structure of the electrons localized on these wires in the 3x2 phase was also probed by ARPES.³⁷ We found four different electronic bands related to the quantum wires within the band gap of bulk SiC. The band structure measured shows, however, only very small dispersions for all the surface-state bands, which suggests that the electrons are well localized without a significant interaction even along the quantum wires. That is, each building block of the wires is rather independent of each other. Thus a Si quantum wire is not 1D in terms of its electrons but is rather 'zero dimensional'.

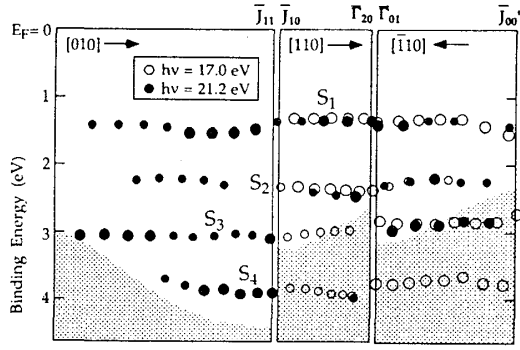


Fig. 11 Experimental dispersion curves for the surface states of the 3x2 phase.³⁷

A peculiar 0D property shows up in detailed STM images of the 3x2 phase as shown in Fig. 10b. At a certain condition, the 3x2 unit cells show random spatial fluctuations (in their structure or charge density). This fluctuation (or disorder) is not dynamic and is frozen even at room temperature. We believe that this fluctuation reflects the 0D character of the surface, which is, however, contradictory with its 1D appearance in STM.³⁵

As demonstrated in the two above examples, just the 1D arrangement of unit cells on surfaces is not a sufficient condition to have exotic 1D electronic systems. That is, we need to find a proper 1D metallic system, where the surface electrons couple indeed one-dimensionally. There have been few candidates of such 1D *metallic* systems on metal and semiconductor surfaces, and the following 4x1-In phase on Si(111) is one of them. This system was recently shown to feature true 1D electronic behaviors, for the first time as a surface system, putting a significant milestone in this line of researches.²⁶

Metallic In chains on Si(111) and charge density wave²⁶ - Initial growth of In on Si(111) results in a variety of 2D phases and one of them has a $4a_0 \times a_0$ ($a_0 = 3.84 \text{ \AA}$) periodicity (the 4x1-In surface hereafter). The 4x1-In surface has a linear chain structure along the x1 direction, which appears as bright stripes spaced $13.3 \text{ \AA}$ apart in the real space images obtained by STM, whose structure is still certain.

The electronic structures of the 4x1-In surface have been studied by both angle-resolved inverse and direct PES which clearly showed that this surface is metallic with three partially filled electronic bands, m_1 , m_2 , m_3 .

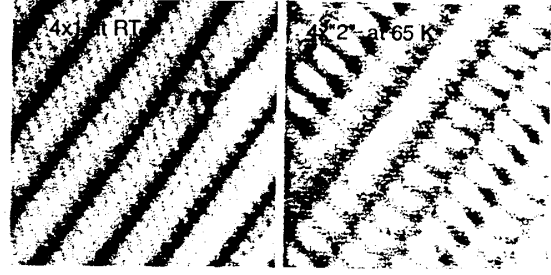


Fig. 12 4x1 and 4x'2' phases for In/Si(111); STM images.

The Fermi contours of these metallic bands are determined in detail by 2D angle-scan PES. The experimentally determined Fermi contours are composed of straight or wavy lines centered along the X-M-X lines of the surface Brillouin zone (SBZ). Their degree of straightness provides a direct measure of the 1D character or anisotropy of each band, since dispersion normal to the direction implies two-dimensionality and also curved contours. In contrast to the substantially curved contours for m_1 and m_2 , m_3 's Fermi contour is perfectly straight suggesting nearly ideal 1D metallic character. Most importantly, this Fermi contour precisely bisect the (4x1) SBZ zone along the chains. Thus a charge density modulation coupled to a lattice vibration of wavelength $2a_0$ along the In chains could lead to a Peierls-like instability with a "nesting vector" of $2k_F = \pi/a_0$ ($a_0 = 3.84 \text{ \AA}$).

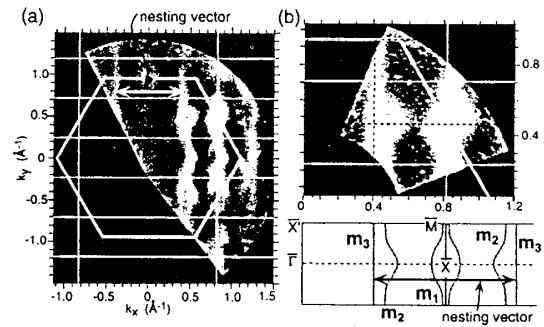


Fig. 13 Experimental Fermi contours of 4x1-In.

The instability of the 4x1 metallic phase is indeed observed when the 4x1-In surface is cooled down to a temperature below $\sim 100 \text{ K}$. The RHEED and LEED patterns at $< 100 \text{ K}$ shows extra x2 periodicity streaks along the chains. These streaks indicate that the charge density and/or the lattice of the surface is perturbed by a $2a_0$ periodicity modulation

along the linear chains, which, however, has a very poor correlation between the chains. Such streaks in diffraction patterns are a characteristic feature of 1D systems.

Accompanying the $4 \times 1 \rightarrow 4 \times 2$ phase transition, the surface electronic structure exhibits drastic changes. The ARPES spectra measured along the linear chains (along Γ -X of SBZ) at RT and at ~ 100 K found that the LT phase is almost semiconducting without any electronic states crossing the Fermi level. Thus, the transition from the 4×1 to the 4×2 phase is obviously a metal-nonmetal transition as expected from Peierls instability.

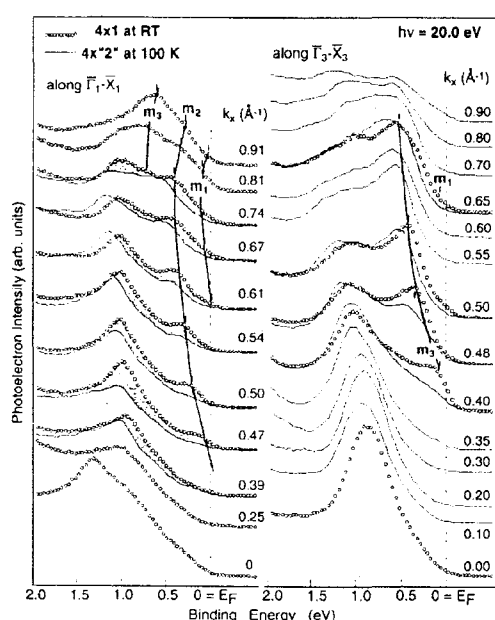


Fig. 14 ARPES spectra for the 4×1 and 4×2 -In surfaces.

Further, the charge density modulation induced by Peierls instability can be observed directly by STM, which maps the local surface state densities. The STM image of the 4×2 -In surface taken at ~ 65 K shows a remarkable difference from that of RT featuring a pronounced $2a_0$ -periodicity modulation of surface charge along the linear chains. This is due to the frequent phase mismatching of the $x2$ modulation between the neighboring chains as shown in Fig. 12. This manifests the 1D nature of the charge density modulation observed.

It is now very clear that we have found a unique

1D CDW transition on solid surfaces, which is composed of quantum wires 'self-organized' on a 2D lattice. Up to now, the real-space observation of the CDW in quasi-1D materials was extremely limited to a very recent report on a bulk organic material with incommensurate CDW (CDWs have been frequently imaged in 2D CDW systems). However due to the great advantage of a well-ordered surface system for STM imaging, the present observation has far more clarity and enables more detailed study of the spatial fluctuations of CDW, an essential aspect of 1D systems. The direct real space observation should provide a unique test case of the microscopic theories for CDW ground states, fluctuations, and excitations in 1D.

For the known bulk quasi-1D materials systems, finite interchain interactions ultimately produce 3D ground states. In the present case of a surface system, an evidence for finite 2D interchain coupling is observed. The lack of 3D interaction in the present system may result in more fundamental differences between the surface 1D materials and other bulk 1D materials through, most probably, the enhanced fluctuations. We note that the ratio of the estimated band gap ($50 \sim 150$ meV) to the transition temperature times the Boltzmann constant is ~ 10 and is thus much larger than simple mean field theory would predict. This ratio is one of the largest among the known 1D CDW systems and fluctuations in 1D is known to suppress the phase transition temperature much lower than predicted by the simple mean field theory.

IV. Conclusions

The present finding of a new type of one-dimensional Peierls materials extends the horizon of the low-dimensional materials science significantly. Many other one-dimensional systems could be found from the anisotropically grown adsorbate systems on various solid surfaces. It can also be suggested that the developing technique of atom manipulation with STM can tailor various types of artificial one-dimensional systems on solid surfaces. These new and interesting materials systems are expected to provide not only the exotic one-dimensional physical properties, but important building blocks for the nanometer-scale electronic and magnetic device technology. Finally it should be noted that detailed electronic structure

studies are of prime importance in finding really 1D materials on surfaces along with microscopy investigations. It is urgent task to develop proper techniques to study the transport, optical and magnetic properties of such surface 1D materials systems.

References

- ¹ A. Zangwill, *Physics at Surface* (Cambridge University Press, 1988).
- ² H. Luth, *Surfaces and Interfaces of Solid Materials, Third edition* (Springer-Verlag, Berlin, 1995).
- ³ 塚田 捷、表面物理入門、東京大学出版会 (1989).
- ⁴ V. G. Lifshits, A. A. Saranin and A. V. Zotov, *Surface Phases on Silicon* (Wiley, Chichester, 1994).
- ⁵ R. I. G. Uhrberg and G. V. Hansonn, *Critical Reviews in Solid State and Material Sciences* **17**, 133 (1991); G. V. Hansonn and R. I. G. Uhrberg, *Surf. Sci. Rep.* **9**, 197 (1988).
- ⁶ D. Hanemann, *Rep. Prog. Phys.* **50**, 1045 (1987).
- ⁷ R. A. Wolkow, *Phys. Rev. Lett.* **68**, 2636 (1992).
- ⁸ P. Krüger and J. Pollmann, *Phys. Rev. Lett.* **74**, 1155 (1995).
- ⁹ H. W. Yeom *et al.*, *Surf. Sci. Lett.* **340**, L983 (1995); *Surf. Sci.* **341**, 328 (1995); *Phys. Rev. B* **54**, 4456 (1997); X. Chen, H. W. Yeom *et al.*; *J. Electron Spectrosc. Relat. Phenom.* **80**, 147 (1996).
- ¹⁰ H. W. Yeom *et al.*, *Surf. Sci. Lett.* **321**, L177 (1994); *Phys. Rev. B* **53**, 1948 (1996); *Phys. Rev. B* **55**, 15669 (1997).
- ¹¹ A. A. Baski, C. F. Quate, and J. Nogami, *Phys. Rev. B* **44**, 11167 (1991).
- ¹² H. W. Yeom *et al.*, *Surf. Sci. Lett.* **381**, L533 (1997); L. Patthey *et al.*, *Phys. Rev. Lett.*, **75**, 2538 (1995).
- ¹³ X. R. Qui and M. G. Lagally, *Science* **278**, 1444, (1997); P. J. Bedrossian, *Phys. Rev. Lett.* **74**, 3648 (1995).
- ¹⁴ G. Grüner, *Density Waves in Solids* (Addison-Wesley, Reading, 1994).
- ¹⁵ H. Namba *et al.*, *Phys. Rev. Lett.* **71**, 4027 (1993); J. E. Ortega *et al.*, *Phys. Rev. B* **49**, 13859 (1994).
- ¹⁶ K. Tanaka, *Jpn. J. Appl. Phys.* **32**, 1389 (1993); E. Bertel and J. Lehmann, *Phys. Rev. Lett.* **80**, 1497 (1998).
- ¹⁷ A. Biedermann *et al.*, *Phys. Rev. Lett.* **76**, 4179 (1996).
- ¹⁸ P. W. Murray *et al.*, *Phys. Rev. Lett.* **80**, 998 (1998).
- ¹⁹ X. Chen, F. Wu, Z. Zhang, and M. G. Lagally, *Phys. Rev. Lett.* **73**, 850 (1994).
- ²⁰ Ch. Park *et al.*, *J. Vac. Sci. Technol. B* **12**, 2049 (1994).
- ²¹ K. Miki *et al.*, *Surf. Sci.* **421**, 397 (1999).
- ²² A. A. Baski, J. Nogami, and C. F. Quate, *Phys. Rev. B* **44**, 11167 (1991); M. M. R. Evans and J. Nogami, *Phys. Rev. B* **59**, 7644 (1999).
- ²³ P. Soukiassian *et al.*, *Phys. Rev. Lett.* **79**, 2498 (1997).
- ²⁴ V. Derycke *et al.*, *Phys. Rev. Lett.* **81**, 5868 (1998).
- ²⁵ 渡邊 聡、日本物理学会誌 **53**, 421 (1998).
- ²⁶ H. W. Yeom *et al.*, *Phys. Rev. Lett.* June 14 (1999).
- ²⁷ W. Widdra *et al.*, *Phys. Rev. Lett.* **80**, 4269 (1998).
- ²⁸ S. Hüfner, *Photoelectron Spectroscopy* (Springer, Berlin, 1995).
- ²⁹ E. W. Plummer and W. Eberhardt, *Adv. Chem. Phys.* **49**, 533 (1982).
- ³⁰ J. Osterwalder, *Surf. Rev. Lett.* **4**, 391 (1997).
- ³¹ R. I. G. Uhrberg, E. Landemark, and Y.-C. Chao, *J. Electron Spectrosc. Relat. Phenom.* **75**, 197 (1995).
- ³² C. S. Fadley, in *Progress in Surface Science*, edited by S. G. Davidson (Pergamon, NY, 1984); D. P. Woodruff and A. M. Bradshaw, *Rep. Prog. Phys.* **57**, 1029 (1994).
- ³³ H. W. Yeom, *Surf. Sci.* **415**, 299 (1998).
- ³⁴ G. Brocks, P. J. Kelly, and R. Car, *Phys. Rev. Lett.* **70**, 2786 (1993).
- ³⁵ S. Hara *et al.*, *Surf. Sci. Lett.* **421**, L143 (1999).
- ³⁶ H. W. Yeom *et al.*, *Phys. Rev. B* **56**, R15525 (1997).
- ³⁷ H. W. Yeom *et al.*, *Phys. Rev. B* **58**, 10540 (1998).