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Current Opinion in Solid State and Materials Science 4 (1999) 429–434

Current Opinion in
Solid State &
Materials Science

Atomic imaging of macroscopic surface conductivity

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Abstract

Scanning tunneling microscopy (STM) enables direct imaging of surface-state bands, through which electrical conduction occurs, confirmed by direct measurements with the four-point probe method. STM images also exhibit voltage drops along a surface due to electrical resistance of the surface states (scanning tunneling potentiometry). Scanning micro-four-point probes and multi-tip STM are newborn techniques for much more direct mapping of the conductivity. Such capability of imaging provides direct insights on carrier scattering at atomic scales. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Since quite large amounts of knowledge on atomic/electronic structures of semiconductor surfaces, especially silicon ones, are now accumulated [1], this is an opportune time for correlating the structures with their physical properties such as electronic transport. Recalling the history of modern surface physics, electrical conduction near semiconductor surfaces was one of the most important subjects around the 1950s since the invention of point-contact transistors. For lack of experimental techniques in those days to directly access the surface structures and to prepare well-defined surfaces, understanding of the phenomena remained quite limited and speculative. Nowadays, however, we have much more sophisticated and versatile surface-sensitive techniques such as scanning tunneling microscopy (STM) and photoemission spectroscopy (PES) in ultrahigh vacuum (UHV), so that the *surface transport* phenomena can be understood in relation with atomic-scale structures of surfaces.

In fact, it was demonstrated quite recently that electrical conduction through *surface-state bands* is actually detectable with well-ordered *surface superstructures* (reconstructed surfaces) on silicon crystals [2]. Surface-state bands inherent in the surface superstructures are unique two-dimensional (2D) electron systems localized only at the topmost atomic layers. This should be distinctly contrasted to the conventional 2D electron-gas (2DEG) systems formed at surface-inversion layers (surface space-charge layers) or heterojunctions. The latter electron systems are bulk-state electrons confined in 2D layers as thick as 10–100 nm by band bending, while the surface-state bands have atomic 'thickness' and their own characters independent of the bulk-state bands. Electronic transport through surface-state bands, therefore, can have novel properties, especially when combined with atomic-scale structural modifications on surfaces.

Recent advancements are reviewed in this article about studies on the surface-state electrical conduction, especially atomic-resolution imaging of the transport phenomena is stressed, demonstrating an advantage in surface-science techniques over conventional transport measurements. Future prospects on newborn techniques for investigating local surface transport, micro-four-point probes and multi-tip STM, are also discussed.

2. STM imaging of surface-state conduction

When two electric leads (e.g. outer probes in linear four-point probe measurements as illustrated in Fig. 1a) are connected to a surface of a semiconductor crystal with a macroscopic distance and a voltage is applied between them, the current flows through three channels on/in the crystal; (1) surface-state bands on the topmost atomic layers, (2) bulk-state bands in a surface-space-charge layer under the surface, and (3) huge bulk-state bands in the inner crystal. To measure the electrical conductivity through the surface-state band, one should carefully eliminate the contributions from the underlying space-charge

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PII: S1359-0286(99)00048-0

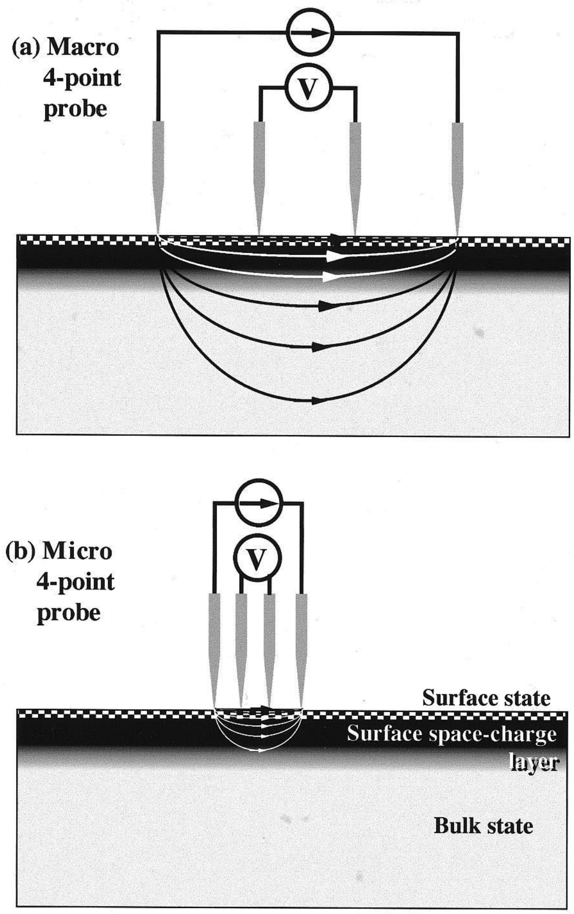

Fig. 1. Linear four-point probes in (a) macroscopic and (b) microscopic spacings, with schematic illustrations of current flow near a semiconductor surface.

layer and bulk; quite a large fraction of the current tends to flow through the interior bulk in most cases.

Surface-state electrical conduction has been confirmed on a Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag surface superstructure, induced by one monolayer (ML) Ag adsorption on Si surface. This surface has a parabolic surface-state band crossing the Fermi level. Such a free-electron-like electronic state is visualized in low-temperature STM images in a form of so-called *electron standing waves* or *Friedel oscillations* [**3,*4,*5]. Fig. 2 shows an STM image of the $\sqrt{3}\times\sqrt{3}$-Ag surface taken at 6 K (though the 7×7 clean domains partially remain, because of a Ag coverage smaller than 1 ML) [6]. In the $\sqrt{3}\times\sqrt{3}$-Ag domains, fine periodic corrugations are seen, corresponding to the $\sqrt{3}\times\sqrt{3}$-periodicity [7]. Additionally, one can see standing wave patterns superimposed near step edges (A) and domain boundaries (B). In a small domain on the upper right, surrounded by steps and domain boundaries, a complicated concentric interference pattern is observed, while near the straight step edges and domain boundaries, the interference patterns are parallel to them. Domain boundaries and atomic steps act as a potential barrier for the surface-state electrons, so that the reflected waves and incident waves interfere with each other to make the standing waves. By changing the bias voltage in STM imaging (in other words, by probing different energy levels), the wavelengths of the observed standing waves changes according to a dispersion relation of the surface-state band [6]. This is an evidence for the wave patterns due to the electronic nature, rather than geometric undulation. In this way, the $\sqrt{3}\times\sqrt{3}$-Ag surface is shown to have an extended surface electronic state (which is mainly composed of Ag 5p orbitals [*8,*9]), which contributes to the electrical conduction

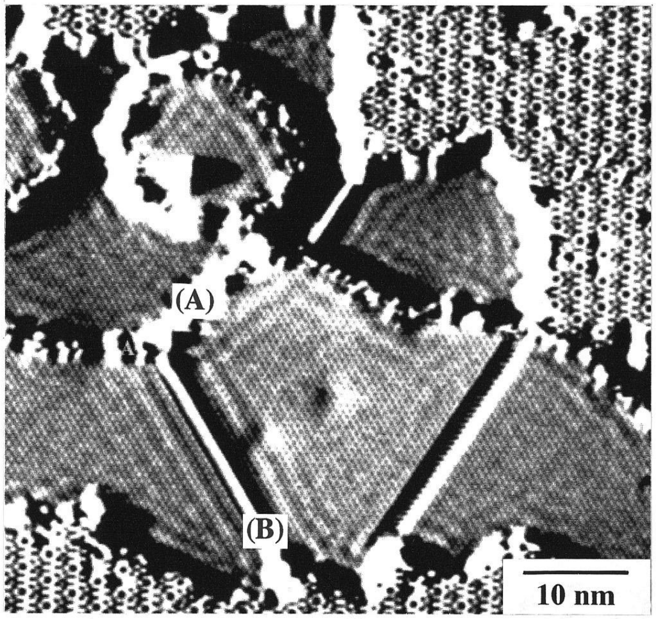

Fig. 2. An empty-state STM image of a Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag surface (partially the 7×7 clean domain remains) taken at 6 K, showing electron standing waves. The tunneling current is 0.5 nA with sample bias of 0.75 V. Reprinted from Physical Review 1999;B59:2035–9. Copyright 1999, with permission from the American Physical Society, [6].

parallel to the surface. An important and interesting question here is, what is the transmission coefficient of electron wave function at such boundaries? Although some papers assumed the step edge as a hard wall for the surface-state electrons (that is, the transmission coefficient is zero) [*4,*5,*10,11,12], it should be questioned, because it governs an important parameter, the mobility of surface-state carriers. It will be certain from Fig. 2 that the carrier mobility is lowered by severe carrier scattering by the step edges and domain boundaries. But how much lowered? The mobility of the surface-state electrons on the $\sqrt{3}\times\sqrt{3}$-Ag surface is actually measured to be lower than in the bulk crystal by two orders of magnitude [13].

On the other hand, in the 7×7 clean domain where no standing wave patterns are observable, the dangling-bond state, which mainly contributes to STM images, is not an extended state, but is localized on the respective Si atoms on the topmost layer. This is the reason for no observable standing waves in spite of its metallic character. Because of this localized nature, as mentioned below, the surface-state conductivity through the dangling-bond state on the 7×7 clean surface is measured to be much lower than that of the $\sqrt{3}\times\sqrt{3}$-Ag surface by four orders of magnitude [**14].

In order to confirm the surface-state electrical conduction, conductivity measurements were done in situ in UHV by four-point probe method with macroscopic probe spacings (ca. 10 mm), combined with electron diffraction to monitor the surface structures, valence-band PES for analyzing the surface electronic states, and also core-level PES for measuring the band bending beneath the surface to estimate the conductivity of the surface space-charge layer [2]. Very small amounts (around 0.01 ML) of deposited atoms of monovalent metals (noble and alkali metals) adsorb individually on the $\sqrt{3}\times\sqrt{3}$-Ag surface, as an example shown in Fig. 3 [15], which is called '2D adatom-gas phase (2DAG)' [16]. Such 2DAG are found to enhance the surface conductivity [17]. From photoemission measurements for valence bands and core-level, it turns out that the adatoms in the 2DAG donate their valence electrons into the surface-state band of the $\sqrt{3}\times\sqrt{3}$-Ag substrate to enhance the surface-state conductivity [2,13,17,18]. By increasing the coverage of the 2DAG up to around 0.15 ML, the adatom gas nucleates two-dimensionally and arranges to make a new order, a $\sqrt{21}\times\sqrt{21}$ periodicity. The $\sqrt{21}\times\sqrt{21}$ superstructures are commonly made by monovalent-atom adsorptions on the $\sqrt{3}\times\sqrt{3}$-Ag surface, and commonly have very high surface conductivities [2,19–21]. The reason for the high conductivity is again turned out by photoemission spectroscopies that new dispersive metallic surface-state bands are created inherent in the $\sqrt{21}\times\sqrt{21}$ superstructures, while the surface-space-charge-layer conductance is suppressed [2,18,19]. In this way, the surface-state electrical conduction has been experimentally confirmed on the Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag surface, whose sheet conductance is of the order of 10^{-4} S/square, measured by macroscopic four-point probes.

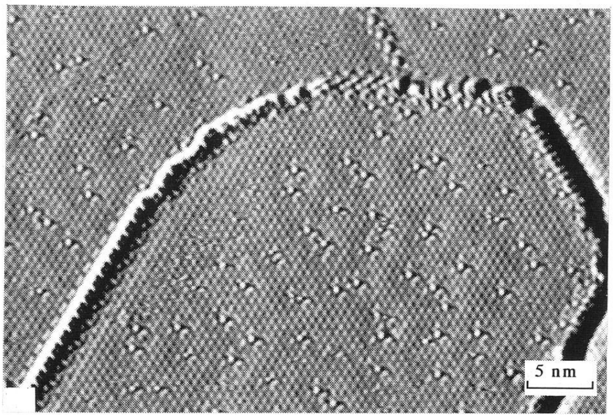

Fig. 3. STM image of Ag 2DAG on the Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag surface at 70 K. Reprinted from Surface Science 1998;408:146–59. Copyright 1998, with permission from Elsevier Science, [15].

3. Scanning tunneling potentiometry

When electrical current flows along the surface, a voltage drop should occur due to its resistance. Such a voltage drop was actually detected by STM (scanning tunneling potentiometry) on surfaces of resistive alloys [22,23] and *pn* junctions [24,25]. Recently a similar technique combined with nano-scale structure fabrications by an STM tip was applied to the Si(111)-7×7 clean surface for measuring its surface-state conductivity [**14]. Heike et al. first fabricated insulating trenches of about 10-nm wide on the surface, by applying a relatively high bias voltage with a high tunneling current in the STM. After that, they observed such a structured surface in a conventional STM mode. Fig. 4a shows a half-closed tape-shaped pattern, surrounded by the insulating trench. The apparent height of the surface inside the tape becomes lower (darker) (by ~0.2 nm) as the STM tip approaches the closed-end of the tape. This result is interpreted as follows: the electrons tunneled from the tip flow along the tape through the surface-state of only the region restricted by the trench, when the tip is positioned inside the tape, because, due to a Schottky barrier between the dangling-bond surface-state and the bulk-state, the current is forced to travel along the surface for a while before leaking into the bulk-state. So a voltage drop occurs along the tape due to a finite resistance of the surface-state, as measured in Fig. 4b. By comparing this voltage drop along the tape with the calculated one, using an equivalent-electrical-circuit model (shown in the inset), they deduced the sheet conductance of the dangling-bond surface-state on the 7×7 surface to be 8.7×10^{-9} S/square. This value is much smaller than that previously obtained by a point contact method by Hasegawa et al. [26] or an AC conductance obtained by electron-energy-loss spectroscopy by Persson et al. [27]. Heike et al. [**14] suggest that this discrepancy arises from a fact that the method of Hasegawa et al.

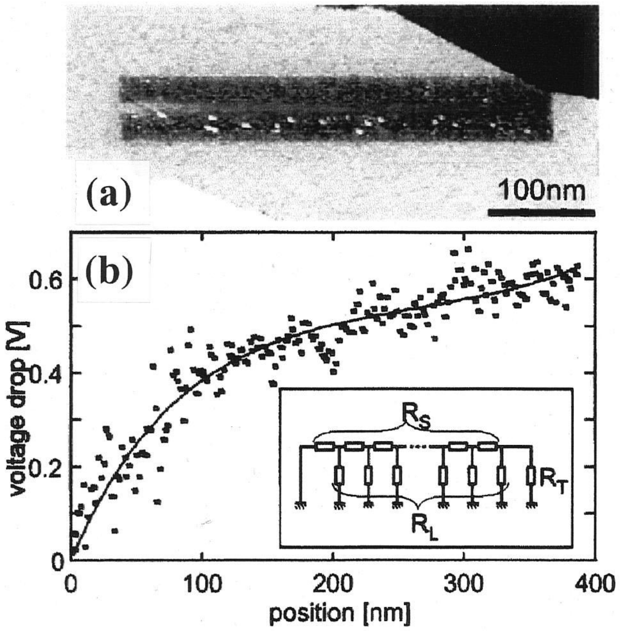

Fig. 4. (a) STM image of a Si(111)-7×7 clean surface with current restriction in a tape-shaped pattern surrounded by insulating trenches. (b) Voltage drop measured along the tape, together with the simulated one (solid line). Reprinted from Physical Review Letters 1998;81:890–3. Copyright 1998, with permission from the American Physical Society, [**14].

should involve the conductance through the surface space-charge layer as well as through the surface states, while Heike's method picks up only the surface-state conductance. This method, however, seems to be applicable only to surfaces having a fairly large resistance, enough to produce the image contrast due to the voltage drop.

4. Micro-four-point probes and multi-tip STM

The four-point probe method enables more direct measurements of conductivity. A group at Mikroelektronik Centret (MIC) of the Technical University of Denmark (DTU) has developed scanning micro-four-point probes with probe spacings down to 2 μm for mapping local conductivity distribution [28]. By reducing the dimension of the probe, as shown in Fig. 1b, a larger fraction of current will flow near the surface, resulting in a more surface-sensitive measurement than by macroscopic four-point probes (Fig. 1a). Such probes are utilized in UHV to measure the surface-state conductivity of the Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag surface, combined with a technique to control the step configuration on the surface [29]; by observing the probes and sample surface by in-situ scanning electron microscopy, the probes are positioned on a large flat terrace, as shown in Fig. 5, where only a few atomic steps run between the inner probes. The sheet conductance measured in this way is larger by nearly an order of magnitude than that measured with macroscopic four-point probes [30]. This result may come from the enhanced surface sensitivity (Fig. 1b) and also from the reduction of carrier scattering by step edges.

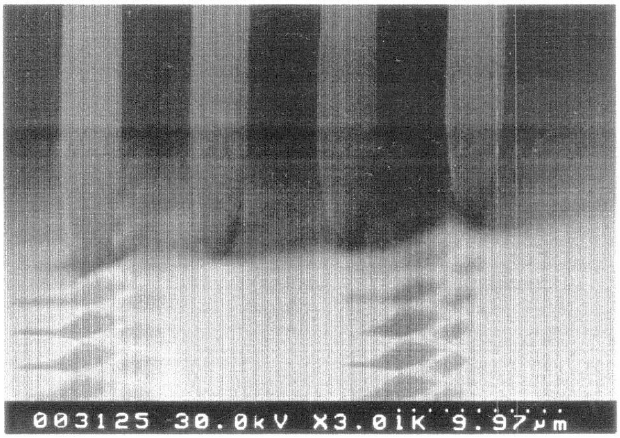

Fig. 5. A scanning electron micrograph showing a micro-four-point probe contacting to the Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag surface with step bunching in UHV.

In order to measure the local conductivity in nanometre-scale regions, several groups are constructing multi-tip STMs in which the tips are utilized as nano-probes to measure local electric properties. The usefulness of double-tip STM is already theoretically discussed [31]. The first trial to make such an STM was done with electrically-isolated two tips mounted on a single scanning head, so that probe spacing could not be changed [32]. A machine with independently driven double-tips is constructed by Aono et al. [*33], in which the tips can be brought together as close as about 100 nm.

These microscopic and nanoscopic probes will be very powerful tools to clarify the carrier-scattering effects of step edges and domain boundaries on surfaces, and also to detect anisotropy in surface conductance of anisotropic superstructures. They are also applicable to measuring the transport properties of nano-scale objects individually such as carbon nanotubes and atomic chains.

5. Conclusions

Direct experimental evidence for the electrical conduction through the surface-state bands, inherent in the surface superstructures, has been given for several systems with the aid of the most sophisticated surface-science techniques such as STM and PES, and also a newborn technique of micro-four-point probes. These studies will trigger more systematic investigations on the electronic transport properties of such an ultimate 2D-electron system, where the correlation with atomic arrangements on surfaces is of essential importance. For example, a recent paper reports that a Si(111)-4×1-In superstructure has a unique one-dimensional metallic surface-state, exhibiting a Peierls-like transition [34]. Surface-state conductance measurements of such a system will reveal a non-Fermi-liquid nature. For that, in-situ measurements at low temperatures under a magnetic field in UHV with atomically controlled sample surfaces are strongly desired. Furthermore, by utilizing technology for manipulating the atomic-scale structures on surfaces, we should be able to control the transport properties in novel ways. In addition to the expectation from the viewpoint of fundamental physics of nanometre-scale systems, the transport properties of surface-state bands will be one of the most important subjects in nano-scale device performance.

Acknowledgements

This work has been supported in part by Grants-In-Aid from the Ministry of Education, Science, Culture, and Sports of Japan, especially through those for Creative Basic Research (No. 09NP1201) conducted by Prof. K. Yagi of Tokyo Institute of Technology, and also for an International Joint Research (No. 11694059) with a group of Dr. F. Grey at MIC of DTU. We have been supported also by Core Research for Evolutional Science and Technology of the Japan Science and Technology Corporation conducted by Prof. M. Aono of Osaka University and RIKEN.

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