Surface-State Electrical Conductivity at a Metal-Insulator Transition On Silicon

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(Received 2 June 2003; published 28 June 2004)

A quasi-one-dimensional metallic Si(111)-(4 × 1)-In surface was investigated by a newly developed temperature-variable microscopic four-point probe method combined with *in situ* electron diffraction in ultrahigh vacuum. We have succeeded, for the first time, in detecting directly a surface metal-insulator transition around 130 K as a dramatic change of electrical conductivity through the surface states. An energy gap of ~300 meV at the low-temperature phase, influences of defects and phase locking between the neighboring charge-density-wave chains were elucidated from the temperature dependence of conductivity.

Low-dimensional transport physics has been explored mainly in two-dimensional (2D) electron gas systems formed at buried interfaces such as metal-oxide Si and GaAs/AlGaAs interfaces [1]. Surface-state bands localized in the outermost atomic layers on crystal surfaces, on the other hand, are in their own right ideal 2D systems [2] [or sometimes quasi-one-dimensional (1D) for highly anisotropic surface superstructures [3,4]]. In addition, their atomic arrangements and (local) electronic structures have been revealed by various kinds of surface-sensitive methods with high energy/spatial/momentum resolutions, which can be correlated with transport properties. In spite of these merits, only a few attempts have so far been made to use the surface-state bands for low-dimensional transport physics, simply because of difficulty in directly measuring their electrical conductivity (surface-state conductivity, σ_{SS}) [5–9]. The surface is always in contact with the substrate bulk that has a much larger volume and larger conductance, which easily hampers the measurements of σ_{SS}. The only way to estimate σ_{SS} is, after measuring a total conductivity, σ_{meas}, including σ_{SS} together with that of the substrate bulk, the bulk contribution is estimated by some means and is subtracted from σ_{meas}. For semiconductor crystals, the conductivity of the substrate bulk is composed of two contributions: the conductivity through a surface space-charge layer (σ_{SC}) due to band bending beneath the surface and that through the inner bulk crystal (σ_b). $\sigma_{meas} = \sigma_{SS} + \sigma_{SC} + \sigma_b$. In order to reduce such substrate contributions, insulating substrates [9] or very thin substrates (so-called silicon-on-insulator crystals[8]) have been utilized. These previous techniques, however, have been very complicated, indirect, and thus may contain possible ambiguities.

We have recently developed a four-point probe method with microscopic probe spacing ($\sim \mu$m) to improve the sensitivity to σ_{SS} [10–14]. The measuring current penetrates into the specimen as deep as the probe spacing roughly, which means a relatively higher surface sensitivity as the probe spacing is smaller, though the results still contain some contributions from the substrate. In the present study, in addition to using the microscopic four-point probes (μ4PP), we have utilized a special type of surface space-charge layer of Si crystals, an inversion layer, which electrically isolates the surface region from the underlying bulk. The measuring current is confined within the space-charge layer and surface states only, so that σ_b can be ignored.

A Si(111)-(4 × 1)-In surface superstructure, composed of a massive array of metallic In atomic chains [15], is known to have quasi-one-dimensional metallic surface-state bands [16]. Their Fermi surfaces nearly bisect the (4 × 1)-surface Brillouin zone [16,17], leading to the formation of a 1D charge-density wave (CDW) due to Peierls instability [18]. Actually, it is known to transform into a 8 × ′2′ structure below 130 K, having an energy gap 2Δ at Fermi level (E_F) as revealed by photoemission spectroscopy (PES) [17,19,20]. The 1D Fermi-surface nesting gives the intrachain periodicity doubling (×′ 2′), while the phase locking between the neighboring CDW chains gives the interchain periodicity doubling (×8) [17]. Since, however, the displacement and rearrangement of surface atoms at the low-temperature (LT) phase, revealed by surface x-ray diffraction [21], are much more significant than the lattice distortion expected from the CDW picture, it has been proposed that the phase transition is a structural reconstruction, rather than a CDW transition. A recent paper on the dynamical low-energy-electron diffraction analysis, however, reports negligible displacements of atoms at the LT phase [22]. Electron energy-loss spectroscopy (EELS) [23] and PES [20], on one hand, show a weak metallic character remaining at the LT phase, meaning a possible "pseudoenergy gap" opening. The first-principle calculation could not reproduce a gap opening for the LT phase [24]. Thus, the nature of this phase transition is still under debate. The measurements of σ_{SS} can shed light on this issue.

In the present study, we have succeeded in clearly showing the transition to be a metal-insulator type as a

drastic change in the temperature dependence of σ_{SS}. We have found that the measured conductivity σ_{meas} below room temperature (RT) is dominated by σ_{SS} only. The simultaneous reflection-high-energy electron diffraction (RHEED) has revealed that the insulating behavior occurs when the neighboring CDW chains are locked in phase. We have obtained an unexpectedly large energy gap ($\sim$300 meV) opening at the LT phase and also detected significant influence of defects upon the conductivity. This is the first demonstration of direct measurement of the surface-state conductivity without subtraction of the substrate conductivity, which has opened up an opportunity for a new type of low-dimensional transport physics using a variety of surface states.

We used three kinds of Si(111) crystals of 0.4 mm thick: n-type (nominal bulk resistivity $\rho = 1$–10 cm at RT, P-doping); p-type ($\rho = 1$–30 cm, B-doping); and nondoped ($\rho \sim 1000$ cm), which were vicinal oriented 1.8° off from the (111) surface towards $\pm[11\bar{2}]$ azimuth. A regularly stepped 7×7 clean substrate was prepared according to a method in Ref. [25] to minimize step bunches and kink density. Indium of 1 monatomic layer was deposited on this surface at 450 °C. Then, a well-ordered, regularly stepped, and single-domain Si(111)-(4 × 1)-In surface superstructure was prepared, where the In atomic chains were parallel to the steps. This was checked by *in situ* RHEED in ultrahigh vacuum (UHV) (Fig. 1), and also by scanning tunneling microscopy (STM) separately.

Electrical conductivity was measured *in situ* by the μ4PP method in UHV [26]. The monolithic probe had four cantilevers made of a metal-covered Si chip, which were in line and equidistant from each other with 8 μm spacing [10–12]. By positioning the probe precisely with piezoactuators, the cantilevers made contact to the sample surface very softly. No damage was detected at the contact points by scanning electron microscopy [10]. Thus, the cantilevers do not penetrate the surface-space-charge layer to reach the underlying bulk region. The sample was mounted on a rotary stage, enabling the cantilevers aligning precisely parallel to the array of In atomic chains. The stages for sample and probe were thermally connected to a liquid nitrogen container. RHEED observations could be done simultaneously.

A four-point-probe resistance R was obtained from the gradients of current-voltage (I-V) curves near $I = 0$ A, which is plotted in Fig. 1(a) as a function of temperature. The resistance for the n-type substrate (filled circles) shows almost constant values above 130 K, while it begins to rise steeply with cooling further. It increases eventually by 3 orders of magnitude at 90 K. The RHEED patterns, intermittently observed during the resistance measurements, showed the 4×1 between RT and $\sim$200 K, while weak half-order streaks [indicated by arrowheads in Fig. 1(b)] appeared between 200 and
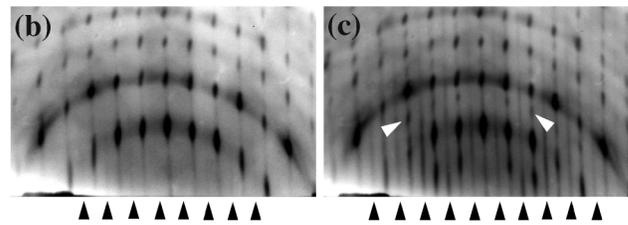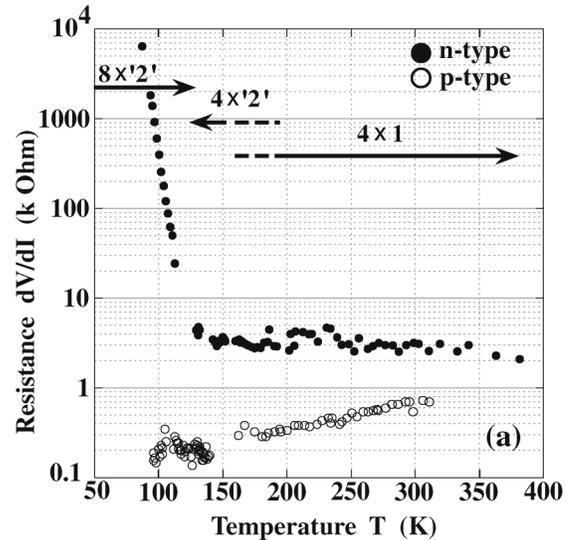

FIG. 1. (a) Electrical resistance of the Si(111)-(4 × 1)-In surface on n-type and p-type crystals measured as a function of temperature. RHEED patterns of (b) $4 \times '2'$ at 150 K and (c) $8 \times '2'$ at 90 K. Black arrowheads indicate half-order streaks, and white ones show the 1/8-th fractional-order spots.

130 K, indicating a $4 \times' 2'$ phase. This means a periodicity doubling along the In atomic chains, while there is no correlation of this doubling between the neighboring chains. Below 130 K, it changed into the $8 \times' 2'$ structure [Fig. 1(c)], indicating a periodicity doubling across the In chains. This is due to finite interchain coupling by the finite band dispersion of surface states across the chains or simply by the Coulomb interaction between the neighboring CDWs [17]. The steep rise in resistance corresponds to the formation of the $8 \times' 2'$ phase, rather than the $4 \times' 2'$ formation. The $4 \times' 2'$ phase, where the 1D CDW is fluctuating along each chain, does not exhibit an insulating behavior in electrical conduction, though the periodicity doubling along the In chains due to a quasi-1D Fermi-surface nesting should make the chain insulating. This is consistent with a conventional picture that the fluctuating CDW phase at the intermediate temperatures exhibits a metallic character [18]. The phase locking of CDW across the chains is necessary for the insulating electrical conduction.

For the p-type crystals, on the other hand, no steep changes in resistance were detected around 130 K as shown by open circles in Fig. 1(a), though almost exactly the same changes in RHEED were observed as for the n-type crystals. Thus, the influence of the surface phase

transition upon the electrical resistance could not be detected for p-type substrates within our experimental resolution.

We attribute this difference between the n and p types to the difference in band bending beneath the surface. The E_F position at surface was close to the bulk valence-band maximum, measured by using energy shifts of a bulk peak in PES. This was irrespective of the bulk doping type, due to a Fermi-level pinning by the surface states. The details will be published elsewhere. This means the surface-space-charge layer to be a weak hole-accumulation layer, or an inversion layer on the n-type substrate, while it is nearly in a flat-band situation for the p-type substrate. Since, then, the inversion layer is separated from the underlying n-type bulk by a depletion layer in between, the measuring current cannot penetrate into the underlying n-type bulk region, resulting in a high surface sensitivity in resistance measurement, because the thickness of the inversion layer is as thin as 0.1–0.5 μm for 1–10 Ω cm crystals [14]. For the p-type substrate, however, the measuring current spreads out into the inner bulk, giving a bulk value, because the bulk region mainly contributes to the conduction. Actually, the gradual change in resistance with temperature for the p type in Fig. 1(a) is due to the temperature dependence of carrier mobility in the bulk Si crystals.

Then, we can ignore the contribution of σ_b for the n-type crystal (and the nondoped one, too), resulting in $\sigma_{\mathrm{meas}} = \sigma_{\mathrm{SS}} + \sigma_{\mathrm{SC}}$, meaning the conduction to be intrinsically 2D. Then, the sheet conductivity σ_{meas} is derived from the measured resistance R by $\sigma_{\mathrm{meas}} = (\ln 2/\pi)R$, which is plotted as a function of the inverse of temperature T for the n-type (solid circles) and nondoped crystals (squares) in Fig. 2. Both crystals show a drastic change in conductivity around 130 K.

Next, in order to elucidate σ_{SS}, we have evaluated σ_{SC} as a function of T. Since we know the E_F positions at the surface and in the inner bulk, we can calculate the band bending and the resulting excess carrier concentration at the surface-space-charge layer (a hole-accumulation layer), using a well-established method by solving the Poisson equation [27]. In this calculation we have involved the T dependences of the surface E_F position that was measured by PES and of the bulk E_F position, and T dependence of the mobility of holes in the space-charge layer [28]. Thus we have obtained σ_{SC} for the n-type crystal, which is plotted by the hatched area in Fig. 2(a). The σ_{SC} is less than 1/3 of σ_{meas} at RT, and steeply drops with temperature lowering, to be much smaller than σ_{meas}. It should be noted here that, for the above estimation of σ_{SC}, diffuse carrier scattering at the surface, which causes a decrease in the carrier mobility, has been ignored. So the above-calculated σ_{SC} is its upper limit; its actual values may be much smaller than those shown in Fig. 2. Thus we can safely say that σ_{SC} becomes negligible below $\sim$200 K, and σ_{meas} is dominated by σ_{SS}

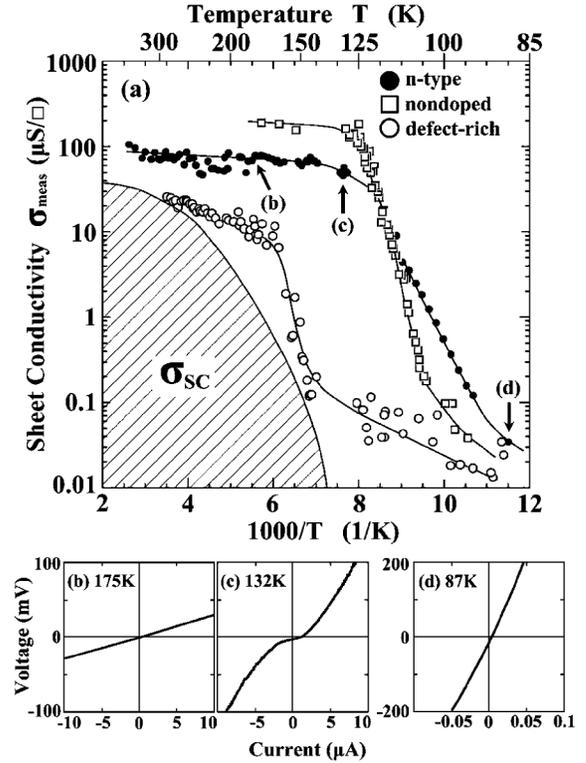FIG. 2. (a) σ_{meas} vs $1/T$ for the pristine (4 × 1)-In surfaces on an n-type (filled circles) and a nondoped crystal (open squares), and for the defect-rich (4 × 1)-In surface (open circles). The curves on the data points are just to guide the eye. The hatched area shows the calculated conductivity of the surface space-charge layer σ_{SC}. (b)–(d) I-V curves at each temperature.

only. In other words, we measure the surface-state conductivity directly, without any subtraction of the contribution of substrate conductivity.

Next we analyze the LT phase. If, as mentioned before, the LT phase is an insulating phase with the CDW gap 2Δ, $\sigma_{\mathrm{SS}} \propto \exp(-\Delta/k_B T)$. The measured conductivity at the lowest temperatures in Fig. 2 is well fitted with this equation for both of the n-type and nondoped crystals, giving $2\Delta \sim 300$ (± 50) meV. This means that we have actually detected a metal-insulator transition in surface states by conductivity measurements. Irrespective of the nature of phase transition (CDW [17] or structural reconstruction [21]), the present results clearly indicate the LT phase (8 ×′ 2′) to be insulating. This denies the EELS and PES results insisting a pseudogap remain at LT [20,23]; this discrepancy may come from inhomogeneous surfaces with partially remaining metallic domains immersed in the insulating phase.

We should be careful of the linear μ4PP measurement of an anisotropic conductor like the present case, however, because σ_{meas} always just gives a geometrical mean of the conductivity along the chains $\sigma_\parallel$ and that across them $\sigma_\perp$, irrespective of the probe alignment with respect to the In-chain direction [29], $\sigma_{\mathrm{meas}} = \sqrt{\sigma_\parallel \cdot \sigma_\perp}$. Therefore, the σ_{meas} includes the temperature

dependences of both $\sigma_\perp$ and $\sigma_\parallel$. As shown in Ref. [29], however, $\sigma_\perp$ at RT comes from the surface-space-charge layer conductivity mainly, and it decays rapidly with cooling as shown in Fig. 2 in the present paper. Therefore, both $\sigma_\perp$ and $\sigma_\parallel$ at LT come from the surface-state bands only, which accordingly should have the same temperature dependence (though the conductivity values themselves are quite different from each other). Therefore, we can say that the energy gap measured here is that along the In chains as well as across them.

But, the energy gap 2Δ thus obtained is 3 to 4 times larger than that estimated by PES [19,20] and that expected from a weak-coupling mean-field theory of CDW [18]. This may suggest a strong electron-phonon coupling and large fluctuation. Actually as shown in STM observations [30], the CDW interacts with the underlying lattice giving a strong locking effect, which is a common feature for a commensurate CDW system like the present case. We should be careful, furthermore, when comparing with the PES result. The energy gap estimation by PES is always based on an assumption of a symmetric gap; the E_F is assumed to locate at the total gap center, and the total gap size is twice the gap measured by PES. This assumption is not yet confirmed. According to the most recent PES measurements [31], furthermore, three metallic surface-state bands change at this phase transition in a complicated way. Thus, to understand the unexpectedly large gap ~ 300 meV for this system, a theory beyond the naive single-band CDW picture would be necessary.

We found nonlinear I-V characteristics around the transition temperature. While the I-V curves at the high-temperature phase and LT phase are straight as shown in Figs. 2(b) and 2(d), it shows a strong nonlinearity only around 130 K as shown in Fig. 2(c); it shows a larger resistance with larger bias voltage. Such a behavior has never been reported for bulk CDW materials [18]. It should be noted here that the CDW sliding mechanism may show an opposite behavior in which the resistance becomes smaller by larger voltage [32]. Our nonlinear characteristic almost disappeared for the defect-rich (4×1)-In surface, as described below. Therefore, the nonlinear I-V characteristic is intrinsic in this phase transition. But we do not yet have a definite explanation for this.

Finally we point out the significant influence of defects that were intentionally introduced by depositing an additional 0.1 monolayer of In atoms on the well-ordered (4×1)-In surface at RT. The conductivity of such a defect-rich surface on the n-type crystal is shown by open circles in Fig. 2(a). It is much lower than that of the pristine (4×1)-In surface over the entire temperature range, and its apparent transition temperature for a steep change of conductivity becomes higher. The role of defects in the phase transition will be discussed in more detail with PES data elsewhere.

In summary, we have succeeded in detecting the metal-to-insulator transition in the surface state by conductivity measurements directly. The LT phase has an energy gap as large as ~ 300 meV, excluding the previous results suggesting a pseudogap opening. The phase transition is not an order-disorder type, rather compatible with a Peierls type with strong electron-phonon coupling.

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