Surface Conductance near the Order-Disorder Phase Transition on Si(100)

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The surface conductance of the Si(100)-(2×1) surface was measured as a function of temperature on a fully depleted Si(100)/SiO_2/Si substrate. The surface-state conductance is surprisingly large and reveals a clear signature of the $c(4 \times 2) \rightarrow 2 \times 1$ order-disorder phase transition of buckled Si dimers on Si(100). Surface scattering increases with decreasing $c(4 \times 2)$ order on the surface.

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The transport properties of solids—their capacity to conduct heat and electricity—have always been a core topic of condensed matter physics [1]. Important discoveries in condensed matter and materials physics are most often associated with novel transport phenomena, frequently encountered in materials of considerable chemical and structural complexity or materials of reduced dimensionality. Ordered surfaces and ultrathin films are a special class of low-dimensional materials that are quantum confined in one dimension but extended periodically in the other two dimensions. Surface science has provided the know-how and means to fabricate and characterize atomically clean surfaces and to manipulate thin film growth and thus presents wonderful opportunities to explore the fundamentals of electronic transport in reduced dimensionality. However, the present understanding of *surface* electronic properties is based on electron spectroscopies and first-principles electronic structure calculations. None of these relates directly to the macroscopic materials properties such as the temperature-dependent electrical conductivity, which so far seemed impossible to measure.

In this Letter, we present temperature-dependent four-point probe conductivity measurements of the Si(100)-(2×1) surface. This reconstructed surface consists of a two-dimensional array of buckled Si dimers atop the bulk-truncated surface (Fig. 1a) [2]. At the lowest measurement temperature (120 K), buckled Si dimers are locked into an "antiferromagnetic" $c(4 \times 2)$ array. As the temperature is raised, the long-ranged $c(4 \times 2)$ order diminishes gradually due to thermally activated flip-flop motions of the Si dimers [2] and/or rapid propagation of phase-shifting defects along the dimer rows [3]. The order-disorder transition is complete near 200 K. This two-dimensional (2D) electron system is characterized by a $\sim$0.5 eV gap separating filled and empty surface-state bands, a total electron density of 6.78×10^{14} cm^{-2}, and an effective mass of $\sim 0.4 m_e$ [2]. The Fermi level is pinned by defect-induced gap states associated with "type-*C*" point defects (Fig. 1b) [4].

Random adsorbates on a thin metal film scatter conduction electrons and increase the electrical resistivity of the film [5,6]. Therefore, in order to measure the transport properties *intrinsic* to a surface or ultrathin film, experiments must be carried out in ultrahigh vacuum (UHV). UHV transport measurements on thin metal films have been reported [7–11], but the temperature dependence of the electrical conductivity has not been studied in the ultimate limit of a reconstructed surface layer. We have utilized bulk Si and ultrathin Si/SiO_2/Si or silicon-on-insulator (SOI) substrates to analyze the relative importance of the various conduction channels near the Si(100) surface *as a function of temperature.* The surface-state conductivity appears surprisingly large and exhibits a metallic temperature dependence between 120 and 300 K. The data furthermore show a clear signature of the $c(4 \times 2) \rightarrow 2 \times 1$ order-disorder transition of buckled Si dimers on Si(100) [2].

Experiments were carried out in an UHV. We employed *n*-type Si(100) bulk wafer (14 Ω cm) and *p*-type

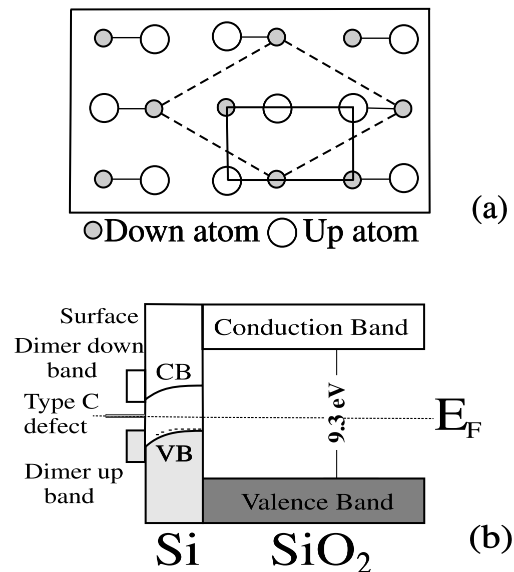

FIG. 1. (a) Top view of the 2×1 dimer array on Si(100). At RT, dimer atoms oscillate up-down, resulting in a time-averaged 2×1 structure (solid line). Dashed lines indicate the primitive unit cell of the $c(4 \times 2)$ structure. (b) Schematic band diagram of the silicon-on-insulator structure including the surface states and the type-*C* defect state (not to scale).

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(100) SOI material (19 Ω cm). The SOI material has a top layer thickness of 900 Å (which is well below the nominal depletion layer width of ≈7000 Å) and was prepared and characterized according to the procedures in Ref. [12]. Ohmic contact pads (2×2 mm^2) were defined by a 10^{15} cm^{-2} phosphorous or boron ion implant on the four corners of a 10×10 mm^2 sample. The sheet resistance was measured according to the van der Pauw method using a dc current source. A well-ordered Si(100)-(2 × 1) surface reconstruction was obtained by repeated flashing to 1300 K in UHV as evidenced with low energy electron diffraction (LEED).

The surface conductance, $\Delta\sigma(T)$, in units of $\Omega^{-1}/\square$, is an excess quantity defined as follows:

$$G(T) = \sigma_b(T) \times d + \Delta\sigma(T), \qquad (1)$$

where $G(T)$ is the square conductance of the sample, d is the thickness of the sample, and $\sigma_b(T)$ is the conductivity of the bulk. $\Delta\sigma(T)$ includes electronic conduction through the surface states and through the space-charge layer beneath the surface and vanishes for an ideally truncated surface with no surface states. The space-charge layer beneath the Si(100)-(2 × 1) surface is a depletion layer due to Fermi level pinning by type-C surface defects at ~0.4 eV above the bulk valence band maximum (Fig. 1b) [4,12].

To obtain $\Delta\sigma(T)$ for Si(100)-(2 × 1), we first measured the square conductance $G_{2\times1}(T)$ of the n-type bulk Si(100)-(2 × 1) sample in UHV from $T \approx 120$ to 300 K. Next, we saturated the clean Si(100)-(2 × 1) surface with O_2 at RT. This procedure destroys the surface reconstruction (as evidenced by a 1 × 1 LEED pattern), eliminates the surface states [13], and creates a nearly flat-band surface according to band bending measurements with Si 2p core level spectroscopy [14]. The conductance of the oxidized sample, $G_{O_2}(T)$, was also measured from 120 to 300 K and we obtained $\Delta\sigma(T) = G_{2\times1}(T) - G_{O_2}(T)$. This difference measurement is prone to large errors if the contact resistances are not exactly reproducible after cooling and heating cycles. The use of ion-implanted contacts is therefore pivotal. To avoid possible hysteresis, we recorded data only during the heating of the sample. In reality, $G_{O_2}(T)$ is slightly less than $\sigma_b(T) \times d$ due to adsorbate-induced surface scattering. We show, however, that this effect is negligible for Si.

Figure 2 shows the conductance of the (2 × 1)-reconstructed bulk Si sample as a function of exposure to O_2 at RT. It shows that a clean reconstructed sample is less resistive than a sample passivated with O_2, in agreement with other RT chemisorption studies [15,16]. The same behavior has been observed for p-type samples [15] and has been explained in terms of space-charge layer conductance [16] or diffuse scattering at the O_2 passivated surface [15]. As we show below, none of these mechanisms accounts for the experimental observations. Instead, the data of Fig. 2 are fully consistent with the presence of a surface-state conduction channel on Si(100)-(2 × 1) that is gradually destroyed by the adsorption of O_2.

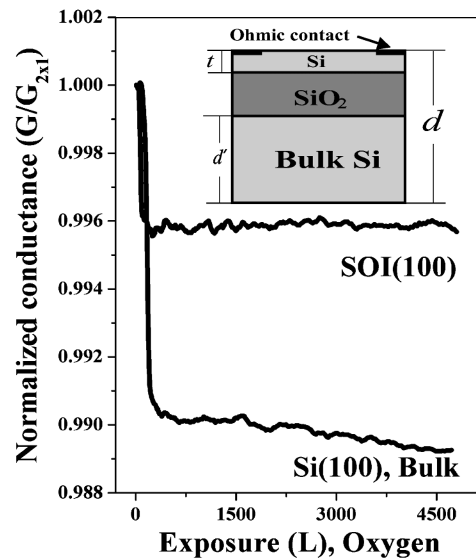

FIG. 2. Conductance of n-type bulk Si(100)-(2 × 1) and p-type SOI(100) during exposure to O_2 at RT. Inset: Side view of the SOI sample with ion-implanted contacts.

In order to separate the surface-state and space-charge layer contributions to the total surface conductance, $\Delta\sigma(T)$, we calculate the space-charge layer contribution, $\Delta\sigma_{sc}(T)$, using Ref. [17]:

$$\Delta\sigma_{sc} = e(\mu_{n,s}\Delta N + \mu_{p,s}\Delta P), \qquad (2)$$

where $\Delta N = \int_o^\infty [n(z) - n_b]\,dz$ and $\Delta P = \int_o^\infty [p(z) - p_b]\,dz$ are the excess densities of electrons (n) and holes (p), respectively, near the surface. Subscripts s and b refer to the surface ($z = 0$) and bulk ($z = \infty$), respectively; $\mu_{n,s}$ and $\mu_{p,s}$ are the surface mobilities. By solving Poisson's equation in the abrupt depletion approximation using Boltzmann statistics and parabolic bands and by introducing the new variables $v(z) \equiv [E_{ib} - E_i(z)]/k_BT$ and $u(z) \equiv [E_F - E_i(z)]/k_BT$, Kingston and Neustadter derived [18]

$$\Delta N = n_b L_D \int_{v_s}^{0} (e^v - 1)/ \mp F(u_b, v)\, dv, \qquad (3)$$

$$F(u_b, v) = \sqrt{2}\sqrt{[\cosh(u_b + v)/\cosh u_b - v \tanh u_b - 1]} \qquad (4)$$

(with a similar equation for ΔP), $E_i(z)$ is the intrinsic Fermi level, $v(z)$ is the band bending [$v_s \approx 0.34$ eV for Si(100)-(2 × 1) at RT], L_D is the extrinsic Debye length, and k_B is Boltzmann's constant. The surface mobility of Si(100)-(2 × 1) was calculated for the majority carriers using the approximate solution of the Boltzmann transport equation for depletion layers [17,19]:

$$\mu_s = \mu_b \left\{ 1 - \frac{(1-r)\lambda_b}{L_D\sqrt{2}} \frac{1 - e^{-|v_s|}}{\sqrt{(e^{-|v_s|} + |v_s| - 1)}} \right\}, \quad (5)$$

where μ_b is the mobility of the majority carrier in the bulk and $\lambda_b \approx (\frac{\mu_{n,b}}{e})\sqrt{(3m^* k_B T)}$ is the bulk mean free path (m^* is the electron effective mass). The phenomenological Fuchs parameter r represents the fraction of specular scattering events [20]. Its temperature dependence depends on the microscopic nature of the surface scattering events, i.e., scattering from surface phonons, ionized impurities, and/or surface roughness. We have calculated the temperature-dependent $\Delta\sigma_{sc}(T)$ for the Si(100)-(2 × 1) surface from Eqs. (2)–(5), taking into account the temperature dependences of the parameters λ_b, L_D, v_s, u_b, μ_b, and n_b for specular ($r = 1$) and diffuse ($r = 0$) surface scattering. Minority carrier contributions have been ignored. The theoretical $\Delta\sigma_{sc}(T)$ is shown in Fig. 3, together with the experimental data $\Delta\sigma(T)$. Irrespective of the precise surface scattering mechanism, $\Delta\sigma_{sc}(T)$ is opposite in sign to the experimental $\Delta\sigma(T)$. This discrepancy increases at lower temperature. Evidently, the surface-state conduction $\Delta\sigma_{ss}(T)$ contributes to the total sheet conductance. It is obtained by subtracting $\Delta\sigma_{sc}$ from the experimental surface conductance, $\Delta\sigma(T)$ (see Fig. 3).

In a previous RT study [15], it was proposed instead that the discrepancy between $\Delta\sigma_{sc}$ and $\Delta\sigma$ is caused by a strongly reduced carrier mobility beneath the O_2-passivated surface due to roughening of the surface during oxidation; i.e., the O_2-passivated surface may not be representative of the ideal flat-band surface. A simple argument shows that this effect is small and does not reverse the sign of $\Delta\sigma(T)$. In the abrupt depletion approximation, extrinsic carriers originating from the 2 × 1 depletion layer (width $\sim L_D$) are trapped in the surface states so that $G_{2\times1} \approx \sigma_b(d - L_D)$. In the limit of completely diffuse scattering ($r = 0$) at the flat-band O_2/Si(100) surface, one obtains $G_{O_2} \approx \sigma_b(d - \lambda_b)$. Since $\lambda_b \ll L_D$ for Si at RT and below, $\Delta\sigma(T) = \{G_{2\times1}(T) - G_{O_2}(T)\} < 0$, in contradiction with experiment. The only plausible explanation for the large conductivity (and sign discrepancy) of the (2 × 1)-reconstructed surface seems to be the presence of a surface-state conduction channel.

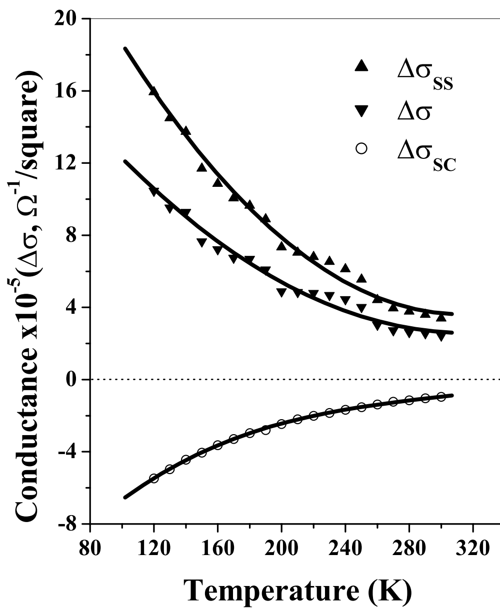

FIG. 3. Temperature dependence of the excess surface conductance according to the space-charge layer calculation, $\Delta\sigma_{sc}(T)$, and according to experiment, $\Delta\sigma$, for the n-type bulk Si(100) sample. The surface-state conductance $\Delta\sigma_{ss}(T) = \Delta\sigma(T) - \Delta\sigma_{sc}(T)$.

A second experiment was carried out to determine the surface-state conductance without resorting to temperature-dependent (and model-dependent) space-charge layer calculations and assumptions about the mobility reduction beneath the O_2-passivated surface. In this experiment, we used a 900-Å-thick, *fully depleted* p-type SOI sample to minimize subsurface conduction (Fig. 2 inset). The resistance between the top layer and bottom substrate was only on the order of 1 MΩ so current does flow through the bottom substrate [21]. However, oxidation of the top layer does not affect the conductance through the substrate beneath the 3800-Å-thick buried oxide. Modeling the SOI as a parallel-plate conductor separated by a nonconducting buried oxide, we thus obtain $G_{2\times1}(T) = \sigma_b(T) \times d' + \Delta\sigma_{ss}(T)$ and $G_{O_2}(T) = \sigma_b(T) \times [d' + t - (1-r)\lambda_b(T)]$, giving

$$\Delta\sigma_{ss}(T) = G_{2\times1}(T) - G_{O_2}(T)\frac{d'}{d' + t - (1-r)\lambda_b(T)}, \quad (6)$$

where t and d' are the thickness of the Si top layer and the supporting substrate, respectively, and r is the Fuchs' specularity parameter of the O_2-passivated surface. Note that $\lambda(T) < t \ll d'$ for $T > 100$ K. The experimental surface-state conductance, $\Delta\sigma_{ss}(T)$, is obtained from Eq. (6) and shown in Fig. 4 using $r = 0$ (diffuse scattering). In reality, r is a model-dependent parameter that varies with temperature, which also makes $\Delta\sigma_{ss}(T)$ somewhat model dependent. However, its most salient feature, i.e., the sharp increase below 200 K is model independent because $d' \gg t, \lambda(T)$.

The experiment clearly shows that the surface-state conduction increases rapidly below ~200 K. We believe that $\Delta\sigma_{ss}(T)$ decreases with increasing temperature as the buckled dimers on Si(100) gradually lose their long-range $c(4 \times 2)$ ordering. The order-disorder transition is almost complete near $T \approx 200$ K [22], which explains why $\Delta\sigma_{ss}(T)$ reaches a minimum (maximum surface scattering). To illustrate this point we also show the intensity of the (3/2, 3/4) spot in LEED as a function of T/T_c as reported in Ref. [22], which reflects the order parameter of the $c(4 \times 2)$ reconstruction. Figure 4 strongly suggests a link between surface-state conductance and structural (dis)order on the surface. Our own LEED patterns also showed a clear $c(4 \times 2)$ superstructure at the lowest measurement temperature (120 K). Above

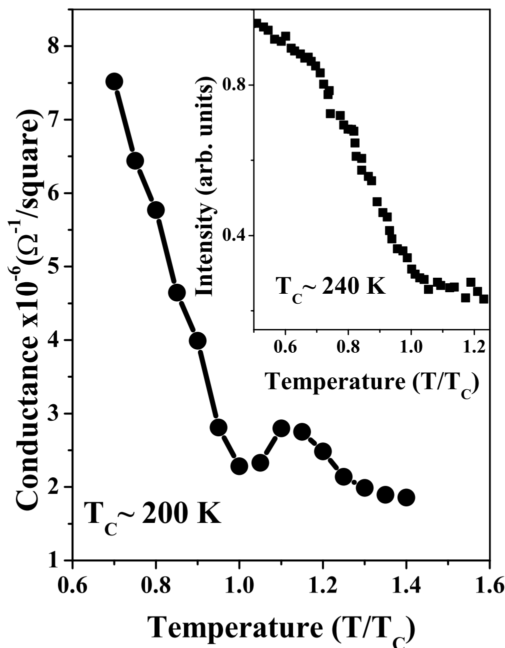

FIG. 4. Experimental determination of the surface-state conductance of (100) SOI, using Eq. (6) with $r = 0$. The intensity of the (3/2, 3/4) LEED spot of the $c(4 \times 2)$ superstructure is taken from Ref. [22].

approximately 200 K, fractional order spots were usually too weak to be observed by eye, which is qualitatively consistent with previous observations. There are other surprises. First of all, the surface-state conductivity is sufficiently large to offset the conductivity reduction in the space charge layer beneath the 2×1 surface. Its magnitude of $\sim 10^{-6}\ \Omega^{-1}/\square$ is comparable to the RT results by Hasegawa for Si(111)-(7×7) (which is probably a 2D correlated metal [23]) using scanning tunneling microscopy point contacts [24]. Second, the temperature dependence of the surface-state conductivity is indicative of metallic behavior whereas the 2×1 and $c(4 \times 2)$ reconstructions have a ~0.5 eV band gap [2]. Electronic transport in this 2D electron system likely involves excitations between the surface-state bands and possibly the type-C gap state (Fig. 1) but evidently, the dominant factor determining the temperature coefficient between 120 and 300 K is the order parameter of the $c(4 \times 2)$ structure.

In summary, the conductivity of the Si(100)-(2×1) surface has been measured as a function of temperature on ultrathin SOI and on bulk Si. The surface-state conductance on SOI and bulk Si shows metallic temperature dependence between 120 and 300 K. Measurements on SOI furthermore show a clear signature of the $c(4 \times 2) \rightarrow 2 \times 1$ order-disorder transition. The decrease of the surface-state conductance up to 200 K is attributed to the gradual demise of long-range $c(4 \times 2)$ order on the surface.

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