Disentangling Surface, Bulk, and Space-Charge-Layer Conductivity in Si(111)-(7 × 7)

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A novel approach for extracting genuine surface conductivities is presented and illustrated using the unresolved example of Si(111)-(7 × 7). Its temperature-dependent conductivity was measured with a microscopic four point probe between room temperature and 100 K. At room temperature the measured conductance corresponds to that expected from the bulk doping level. However, as the temperatures is lowered below ≈200 K, the conductance decreases by several orders of magnitude in a small temperature range and it saturates at a low temperature value of $\approx 4 \times 10^{-8}\ \Omega^{-1}$, irrespective of bulk doping. This abrupt transition is interpreted as the switching from bulk to surface conduction, an interpretation which is supported by a numerical model for the measured four point probe conductance. The value of the surface conductance is considerably lower than that of a good metal.

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Surfaces are ideal model systems for a detailed and quantitative understanding of electron dynamics, many-body effects, and phase transitions and considerable progress has been made in the field over the past few years [1–3]. Most of the experimental results stem from photoemission (angle-resolved or two photon) and scanning tunneling microscopy. In contrast to the case of bulk samples, surface transport measurements have only played a minor role. Recently, however, this situation has changed and several studies of surface conductance have been reported, employing various techniques [4–11]. One promising approach is the use of microscopic four point probes (4pp). Microscopic probes are surface sensitive because the measured bulk resistance is inversely proportional to the probe spacing but the measured surface resistance is independent of the probe spacing. Thus, if the bulk is poorly conductive and the probe spacing small, surface sensitivity can be achieved.

Transport measurements with such microscopic 4pp's have many possible applications. Promising questions which could be addressed are depth profiling of the conducting properties of high T_C and colossal magnetoresistance materials, measurements on actual semiconductor devices, on nanostructures, and in the field of molecular electronics. However, a true quantitative understanding of such measurements is still lacking, even in the simplest case of clean semiconductor surfaces. In this Letter we present a quantitative approach to disentangle bulk, space-charge-layer, and surface-state contributions to the measured conductance. This is done by combining temperature-dependent 4pp measurements with model calculations of the conductance through the bulk and space-charge layers. The ideas are illustrated using the example of Si(111)-(7 × 7).

The Si(111)-(7 × 7) reconstruction has a long history of debate as to its electronic character (for recent references, see Refs. [12–14]). From electron counting it should be metallic but it could instead be insulating because of strong correlations. Transport measurements on this surface have so far not produced a clear result: the reported surface conductance varies by more than 4 orders of magnitude [4–6,8,9,15], it is not clear if the surface conductance is "metallic" in the sense of $d\sigma/dT < 0$ [8] or not [9], and some experiments have even found it, unexpectedly, to depend on the bulk doping [9].

Three p-type Si(111) wafers were used (referred to hereafter as A to C), with resistivities of A: 190 Ω cm, B: 30 Ω cm, and C: 1.3 Ω cm. The 7 × 7 reconstructed surfaces were prepared using a standard high-temperature annealing recipe, resulting in a very sharp low energy electron diffraction (LEED) pattern. Additionally, films of silver were deposited on sample A. The silver evaporator was mounted such that films could be deposited simultaneously with LEED measurements being made. By monitoring the intensities of the truncated bulk and overlayer spots during the evaporation, the coverage, growth mode, and evaporation rate could be estimated using a simple model. For the film discussed below, we estimate the Ag coverage to be nominally 3 monolayers, forming a percolating network of Ag islands with a preferential height of 5 atomic layers covering ≈60% of the surface. Such a growth mode is consistent with previous studies [16–19].

After preparation, the samples were transferred to the variable-temperature measuring stage (95 K to over 300 K). The temperature was controlled by a K-type thermocouple mounted close to the sample. While being held at a stable temperature, a colinear 4pp was approached to the surface. The approach was controlled by an optical microscope. The four probes are made of Au coated SiO_2 [20] and have a separation of 10 μm. The probe-sample contact for the clean surface is non-Ohmic and in the range of 10^4–10^6 Ω, depending on the temperature. It is reproducible and very similar for all four contacts. 4pp measurements were made by scanning the current through the outer two probes and measuring the voltage drop over the inner probes. Depending on temperature, the required current range varied between ≈50 to 500 nA. Many measurements were taken for every given temperature and the error bars reported represent the spread between these data points. More experimental details will be given in a forthcoming publication [21].

Figure 1 shows the results of the measurements on each of the three samples, as well as on the thin Ag film deposited onto substrate *A*. The conductance of the Ag film is always higher than that of the corresponding clean surface (of sample *A*) and it changes only weakly with temperature. For all clean surfaces, however, there is an abrupt change of at least 3 orders of magnitude in the conductance at around 200 K. This cannot be explained by changes in the bulk conductivity since this changes by only a factor of ≈5 in this temperature range. The change is reminiscent of the behavior expected for a phase transition [10] but its origin is altogether different. As shown below, it is due to the switching between surface and bulk conductance caused by the temperature dependence of the carrier density in the space-charge layer. At higher temperatures, the conduction through the space-charge layer is significant and the bulk conductivity dominates the measurement whereas at low temperatures, the space-charge layer becomes very poorly conducting and therefore the bulk is effectively insulated from the surface; thus the surface conductance dominates the measurement.

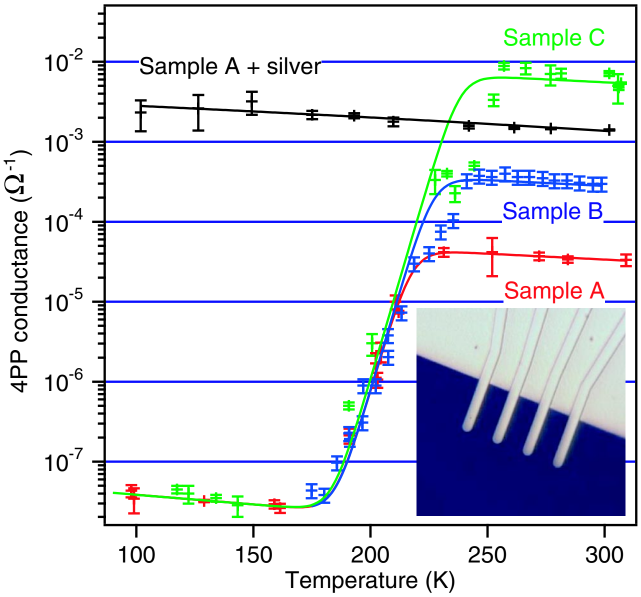

FIG. 1 (color online). Temperature-dependent 4pp conductance of the three Si(111)-(7 × 7) surfaces and of the Ag film. The solid lines are a guide to the eye. The inset shows a typical micro 4pp.

This inference can be qualitatively confirmed from the data in Fig. 1: at low temperatures, where the measurement is suggested to be surface sensitive, the samples show very similar conductivities. This is to be expected since the surface properties should be the same for each sample. Conversely, at higher temperatures where the measurement is attributed as being bulk dominated, the three samples are measured to have different conductances, as expected from the different dopings. Indeed, the measured four point probe conductance $C(4\text{pp})$ at high temperature agrees quantitatively with the expected bulk resistance ρ_b. The two are related by the solution of Poisson's equation for a semi-infinite bulk $C(4\text{pp}) = 2\pi s/\rho_b$, where s is the probe spacing.

This picture is also consistent with the results from the thin Ag film: this percolating network of islands has always a higher conductance than the bulk, thus the measurement is always surface dominated and the data do not show the strong transition that is seen with the (7 × 7) reconstructed surfaces.

While the identification of the low- and high-temperature regimes as surface and bulk conductance appears correct, a definite proof and the quantitative understanding of the data cannot be achieved in a simple way. However, the dynamics of the space-charge layer and the associated effect on the conductivity can be modeled numerically.

Since the bulk doping is known, the bulk position of the intrinsic level relative to the Fermi level can be found as a function of temperature. Also, since the pinning of the Fermi level at the surface is known (in this case it is taken to be 0.65 eV above the valence band maximum after Ref. [22]), the surface potential can be found. From these two parameters, we numerically calculate the band bending V as a function of depth [8,23].

Once the depth dependence of V is known, the carrier densities within the space-charge layer can be calculated. The temperature dependence of the mobility (relative to that of the carrier density) is found to be negligible. It is now straightforward to estimate the conductivity throughout the space-charge layer.

Knowing the temperature and depth dependence of the conductivity, we can calculate the expected 4pp conductance due to the space-charge layer and the bulk by numerically solving Poisson's equation. Note that this model does not include the conductance of the surface as such, i.e., of the conductance truly caused by electronic surface states. Poisson's equation is solved by modeling the crystal as a finite 3D system composed of elemental units. The potential drop between neighboring units is found by means of a simple iterative procedure, and thus the current flowing between units can be calculated by considering the conductivity assigned to each element.

Figure 2 shows the result of the calculation for sample *A*. The calculated 4pp conductance for Si(111)-(7 × 7) shows a strong temperature dependence: at 300 K the calculated and measured conductances agree well. As the temperature

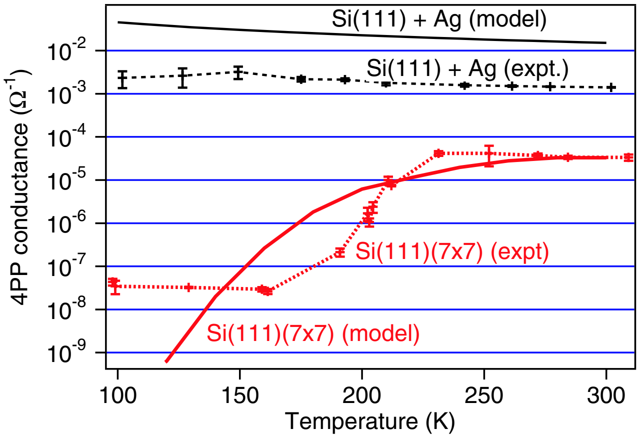

FIG. 2 (color online). Modeled and measured conductances as a function of temperature for sample *A*, both for the clean (7×7) surface and the thin Ag layer on that surface. The (7×7) model includes the bulk and space-charge layer, but the surface-state conductance is excluded.

is lowered, the calculated conductance decreases strongly and so too does the measured conductance, but only down to a value of $\approx 4 \times 10^{-8}\ \Omega^{-1}$ where it saturates.

The temperature dependence of the calculated conductance can be understood as follows: at low temperatures, the Fermi level in the bulk is located close to the valence band maximum, this gives rise to a downward bending of the bulk bands close to the surface, and thus a strong charge depletion (or a weak inversion—depending on the doping strength) layer is formed. Consequently, the conductivity in the space-charge layer is extremely poor. As the temperature is raised, the Fermi level in the bulk moves closer to the intrinsic level, and thus the band bending is reduced. Additionally, the number of carriers is thermally increased and therefore the conductivity across the space-charge region is strongly increased.

At low temperatures, there is a large difference between the model and the data; the model shows that the bulk and space-charge conductance continues to drop below $10^{-8}\ \Omega^{-1}$, while the experimental data all show a plateau in the conductance. This is attributed to genuine surface conductance which is not included in this model, but which dominates the measurement when the space-charge layer isolates the bulk. Thus we can say that at 100 K the surface conductance is $\approx 4 \times 10^{-8}\ \Omega^{-1}$. If we neglect the bulk and the space-charge-layer and regard the surface as an infinite 2D sheet, the sheet conductivity is estimated as $\approx 9 \times 10^{-9}\ \Omega^{-1}$, since for a 2D system the 4pp conductance and sheet conductivity are related by $C(\text{4pp}) = \pi\sigma_S/\ln 2$. It remains possible that this value is affected by a small number of steps and defects between the contacts. Studies on intentionally stepped surfaces have shown that the effect of steps is small. At a high concentration, steps tend to increase the surface conductance [21].

The transition from bulk to surface dominated transport is visualized in current density plots in the low- and high-temperature regime, shown in Fig. 3. These plots have been generated using the *calculated* conductivity for the bulk and the space-charge layer of Fig. 2 to which a two-dimensional surface layer with the *experimental* surface conductivity of $9 \times 10^{-9}\ \Omega^{-1}$ was added. At low temperature the (small) current density is localized at the surface because the space-charge layer is too resistive to allow the current to spread to the more conductive bulk. At high temperature, the current density has a maximum at a depth of $\approx 6\ \mu$m because the higher conductance of the space-charge layer favors a deeper penetration of the current. It also gives rise to a much higher total current density.

From an inspection of the data taken at the lowest temperatures, it also appears that the surface conductivity decreases as the temperature is raised. This would be consistent with a metallic state for which the carrier density is roughly independent of temperature but the mobility is affected by the electron-phonon interaction. The electron-phonon coupling strength for this surface has been inferred from angle-resolved photoemission and found to be strong [14]. In fact, the temperature-dependent lifetime of the photo hole and the conductance are closely related [24] and comparing 4pp and photoemission results would be interesting. However, the electronic states couple mainly to high-energy phonon modes [14]. Therefore, the electron-phonon coupling has only a small effect in the temperature range where our experiment is surface sensi-

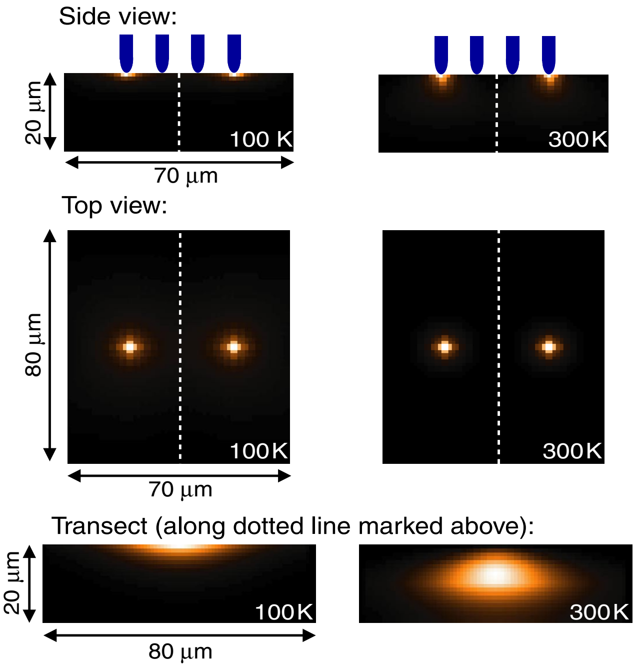

FIG. 3 (color online). Maps of current density from the conductivity models for 100 K (left-hand panels) and 300 K (right-hand panels). The upper panels show the transects along the axis of the probes, the middle panels show the top surface, and the lowest panels are transects through the perpendicular bisector of the probe axis. The plots are scaled such that the highest current density in each plot appears brightest.

tive and the precision presently achievable is insufficient to allow a quantitative comparison to the photoemission results. It has to be emphasized, however, that metallic or nonmetallic behavior, in the sense of having a finite density of states at the Fermi level, cannot be inferred from such a small temperature dependence. Even for a semiconductor, the electron-phonon interaction can give rise to a seemingly metallic temperature dependence of the conductivity in a temperature range where the carrier density is roughly constant.

Another possibility to classify the surface conduction as metallic or nonmetallic is to compare the absolute value of the conductivity to the minimum metallic conduction in two dimensions following the Ioffe-Regel criterion ($3.83 \times 10^{-5}\ \Omega^{-1}$) [8]. According to this comparison, Si(111)-(7×7) is clearly not in the metallic range. This finding appears consistent with a recent temperature-dependent and surface sensitive NMR study of Si(111)-(7×7), which suggested that the surface is close to a Mott-Hubbard-type metal insulator transition [13] and it could also be related to the strong electron-phonon coupling [14].

As pointed out in the introduction, estimates of surface conductivity published elsewhere [4–6,8,9,15] vary from 10^{-4} to $10^{-9}\ \Omega^{-1}$ and our estimate is consistent with the lowest of these. It is particularly interesting to compare our results to those of Tanikawa *et al.* [9] who performed a very similar experiment on n doped Si(111)-(7×7). While their data are in qualitative agreement with ours, i.e., they also observe a strong reduction of the conductivity at low temperatures, their interpretation is different. In particular, they ascribe this to nonmetallic behavior. From applying our model to these samples, however, we believe that the observed temperature dependence of the "surface conductance" can, in fact, be explained by the temperature-dependent conductivity of the space-charge layer.

In conclusion, we have measured the temperature-dependent conductance of Si(111)-(7×7) for three different substrates using a microscale 4pp. By combining these measurements with model calculations, we quantitatively disentangled the contributions of bulk, space-charge layer, and surface states to the measured conductance. At low temperatures our measurement is dominated by the surface conductivity, which can be estimated as $9 \times 10^{-9}\ \Omega^{-1}$ at 100 K. This is below the lowest reasonable value for metallic conductivity and our results are therefore consistent with the hypothesis that Si(111)-(7×7) could be on the verge of a metal to nonmetal transition. Using our approach, it will also be possible to analyze conductivity data from more complicated systems such as novel materials and nanostructures.

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