

Thermal switching of the electrical conductivity of Si(111)($\sqrt{3} \times \sqrt{3}$)Ag due to a surface phase transition

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Corrigendum

Thermal switching of the electrical conductivity of Si(111)($\sqrt{3} \times \sqrt{3}$)Ag due to a surface phase transition

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Our recent paper on the surface conductivity of Si(111)($\sqrt{3} \times \sqrt{3}$)Ag [1] contains an error in the numerical simulation of the space charge layer conductance presented in figure 2(b) of the paper. A new version of the figure is presented here as figure 1.

The incorrect version of this figure suggested that the space charge layer conductivity of Si(111)($\sqrt{3} \times \sqrt{3}$)Ag is very similar to that of the clean Si(111)(7 \times 7) surface but actually this is not the case. The space charge layer for Si(111)(7 \times 7) becomes strongly insulating at low temperatures whereas it is rather conductive over the whole temperature range for Si(111)($\sqrt{3} \times \sqrt{3}$)Ag.

especially since the transition in conductivity is much steeper than one would expect for a mechanism involving the freezing of carriers in the space charge region. However, we would also like to mention an alternative interpretation at this point. The free-electron like surface state on Si(111)($\sqrt{3} \times \sqrt{3}$)Ag is unoccupied at zero temperature because the bottom of the band coincides with the Fermi energy [2]. At finite temperature, thermally excited carriers are present in the surface state band. It is therefore conceivable that the strong change in surface conductivity is caused by the thermal emptying of the surface state band as the temperature is lowered. At low temperature, the surface state band is devoid of carriers and only transport through the bulk and space charge layer can be observed.

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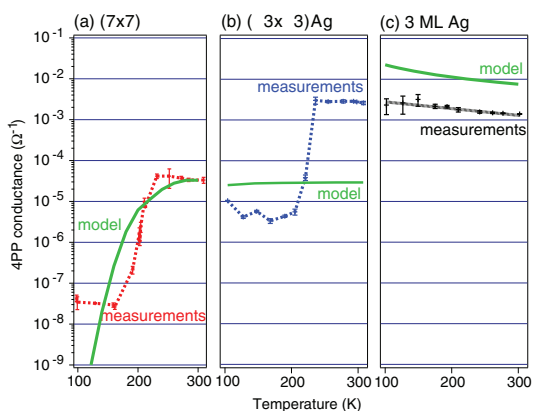


Figure 1. Experimental results (broken lines and markers) together with simulations (solid lines) of the conductance. The simulation in (b) has now been corrected, but the figure is otherwise the same as figure 2 from [1]. The model calculation shows the expected conductance of the bulk and space charge layer in (a) and (b) and for the expected conductance of a 3 ML Ag film with bulk properties in (c).

The error in the calculation of the space charge layer conductivity has an impact on the interpretation of the low temperature measurements. Based on the incorrect calculation, it was concluded that the measurements are always surface sensitive, but this is not the case. In fact, the measured conductance in the low temperature regime is now quite similar to the conductance one could expect for the bulk and space charge layer.

The interpretation of the data as a switching due to the surface phase transition is still consistent with results,

Thermal switching of the electrical conductivity of Si(111)($\sqrt{3} \times \sqrt{3}$)Ag due to a surface phase transition

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Abstract

The temperature-dependent surface conductivity of the Si(111)($\sqrt{3} \times \sqrt{3}$)Ag surface was measured using a microscopic four-point probe. The conductivity was found to undergo a sharp increase of about three orders of magnitude when the system was heated above about 220 K. This strong conductivity change is reversible and attributed to the phase transition which is generally believed to occur on this surface. It is also shown that, in order to find the true surface conductivity, it is necessary to separate it from the contribution of the bulk and space charge layer. In this work, this is achieved by using a finite-element model.

A percolating network of Ag islands on Si(111) was also studied and a much simpler behaviour (compared to that of Si(111)($\sqrt{3} \times \sqrt{3}$)Ag) was found. The temperature-dependent conductivity of this system was found to display typical metallic behaviour. The absolute value of the conductivity is comparable to the value expected by modelling the Ag film as exhibiting the bulk Ag transport properties.

(Some figures in this article are in colour only in the electronic version)

The electronic structure of surfaces, including many-body effects and phase transitions, has recently attracted considerable attraction [1, 2]. The main reason is that the nearly two-dimensional situation at the surface opens up the possibility of testing some fundamental physical concepts related to the interplay of dimensionality and electronic structure. Most experimental work in the field has been carried out using scanning tunnelling microscopy (STM) and angle-resolved photoemission spectroscopy (ARPES). In contrast to the situation in bulk materials, electric transport measurements have played only a minor role, mainly due to their experimental difficulty [3–5].

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In this work, we present measurements of the Si(111)($\sqrt{3} \times \sqrt{3}$)Ag surface, an important model system which has been studied intensely for more than 30 years. In early work, the geometric structure was generally accepted to be described by the ‘honeycomb chained triangle’ (HCT) model; for example, see [6–8]. However, more recent studies suggest that the inequivalent triangle (IET) structure has a lower total energy [9, 10]. The existence of the IET structure has been confirmed experimentally by photoemission spectroscopy [11], x-ray diffraction [12] and reflection high-energy electron diffraction (RHEED) [13]. A considerable amount of controversy still remains. The room-temperature empty state STM images still resemble the HCT structure [14], whilst low-temperature (6 and 62 K) images are consistent with the IET structure [15]. It is generally believed that this is due to a phase transition between the HCT and IET structures, but the character of this transition is not clear. Whilst it has been suggested that a displacive phase transition may occur [12], it is more generally believed that an order–disorder phase transition takes place. Thus, at higher temperatures a rapid switching between the two possible IET domains would result in slow techniques such as STM recording an averaged image that would closely resemble the HCT structure, whereas at lower temperatures the IET fluctuations are frozen out. Very recently, however, the IET structure has also been found in room-temperature STM images, suggesting that a phase transition may not even exist [16].

A look at the surface electronic structure does little to clarify this situation. Until recently, there has been some controversy over the electronic nature of the ($\sqrt{3} \times \sqrt{3}$)Ag surface. Despite many studies with different experimental techniques, the question of whether the surface is semiconducting or metallic was not answered conclusively. First-principles calculations were also unable to provide a clear-cut answer [9, 17–20]. More recent photoelectron spectroscopy studies [21–23] of the Fermi surface and the silicon core levels indicate that exact monolayer coverages of ($\sqrt{3} \times \sqrt{3}$)Ag are semiconducting but, by increasing the Ag coverage by small fractions of a monolayer (Δ), the surface becomes metallic (however there is some disagreement about this [24]). Thus, the pinning of the Fermi level at the surface also shows a strong dependence on the coverage [23]. It has been argued that photoemission could be used to clarify the geometric structure of the surface at room temperature because it is much faster than STM and should therefore reveal the characteristics of a fluctuating IET structure, in particular via a splitting between two surface states at the \bar{K} point of the surface Brillouin zone. This was indeed observed [11], supporting the existence of the IET structure at room temperature, but the result has recently been called into question. Photoemission from a carefully aligned sample reveals no detectable splitting [16], making it impossible to confirm the presence or absence of the IET phase at room temperature.

Since the electronic structure is strongly dependent on the Ag coverage, one would expect a similar dependence of the surface conductivity. The room-temperature measurements performed by Schad *et al* [25] and by Nakajima *et al* [26] reveal that this is indeed the case. However, since changing the Ag coverage is known to affect the Fermi-level pinning at the surface [23], it is difficult to say whether these observed changes in the measured conductance correspond to actual changes in the surface conductivity, or simply to changes in the conductivity of the underlying space charge region. In order to disentangle these effects, a quantitative understanding of the influence of the space charge layer is required.

To summarise, the ($\sqrt{3} \times \sqrt{3}$)Ag surface continues to be of great interest. Although it is generally accepted that this surface undergoes a phase transition, the nature of this transition and the transition temperature remain the subject of some debate, and a corresponding transition in the surface conductivity has never been reported. The surface electronic structure and the apparent surface conductivity appear to be coverage dependent, so one possible explanation for the lack of agreement concerning the transition temperature is that it is similarly dependent on the coverage.

In this paper we report and discuss the temperature-dependent conductivity of Si(111)($\sqrt{3} \times \sqrt{3}$)Ag. As a simple reference system, we also present data for the conductivity of a percolating network of Ag islands on the same Si(111) substrate. The latter system is indisputably metallic, and is not thought to undergo any phase transitions in the temperature range studied (100–300 K).

The Si(111) wafer that was used was p-type doped, with a resistivity of 190 Ω cm. The surface was cleaned by annealing to $\approx 650^\circ\text{C}$ for 24 h, then flashing to $\approx 1250^\circ\text{C}$ for 15 s, cooling rapidly back to $\approx 650^\circ\text{C}$, and then slowly back to room temperature. After this preparation, a very sharp 7×7 reconstruction was observed using low-energy electron diffraction (LEED).

After characterization of the initial clean surface, films of silver were deposited at room temperature. The evaporator was mounted such that silver could be evaporated and LEED measurements made simultaneously. By monitoring the intensities of the Si(1×1), Si(7×7) and Ag(1×1) spots during evaporation, the coverage, growth mode and evaporation rate could be estimated using a simple Monte Carlo model. After deposition for 180 s (or at a nominal coverage of three monolayers), this model indicates that the surface was covered by a network of Ag islands with a preferential height of five monolayers, which just exceeded the percolation threshold. The result from our model is consistent with the available STM, optical and photoelectron diffraction (PED) measurements [27–30].

Following this preparation, a further annealing cycle produced the ($\sqrt{3} \times \sqrt{3}$)Ag reconstruction. This surface has been studied extensively and thus the advice on its preparation is plentiful [12, 13, 16, 21–23, 26, 29–32]. To summarize this work, the ($\sqrt{3} \times \sqrt{3}$)Ag reconstruction can be formed at temperatures from 320°C [30] to 600°C . Thus, the preparation was performed across this temperature range, and the surface checked using LEED. The sharpest LEED patterns were formed following annealing at temperatures between 500 and 600°C , which agrees with the findings of Crain *et al* [23], and is thought to correspond to accurate single-monolayer coverages (compared to the $1 + \Delta$ coverages observed after lower-temperature anneals). Thus, the measurements performed in this paper are made using an annealing temperature of $550 \pm 30^\circ\text{C}$.

In order to perform the transport measurements, the sample was transferred to the variable-temperature measuring stage. The temperature was adjusted using a variable-power liquid nitrogen cryostat and a small filament heater with control feedback provided by a K-type thermocouple mounted close to the sample. Using this setup, the sample could be kept at a constant temperature in the range 95 K to over 300 K. Whilst being held at a stable temperature, a collinear four-point probe (supplied by Capres A/S [33]) was moved towards the surface. The four-point probes were made of Au-coated SiO₂ and had a probe separation of 10 μm (see the inset of figure 1).

Figure 1 shows the results of the measurements on each of the three surfaces. The measurements on the clean Si(111)(7×7) surface and on the Si(111)($\sqrt{3} \times \sqrt{3}$)Ag surface both show a strong transition of several orders of magnitude across this temperature range. The transition in the conductance of the clean Si(111)(7×7) is quite sharp and occurs at about 200 K, whilst the transition of the Si(111)($\sqrt{3} \times \sqrt{3}$)Ag surface is somewhat sharper, and at about 220 K. The measurements on the Ag island film do not show any strong transition, but instead display a weakly decreasing conductivity across this temperature range. Also, the absolute values of the measured conductance of the clean Si(111)(7×7) sample are relatively low, and this is especially notable at low temperatures.

Each of these data series has been repeated several times, and measured by both increasing and decreasing the temperature. In the case of the clean Si(111)(7×7) surface, the measurements are accurately repeatable. For the Ag island film, the repeatability is quite

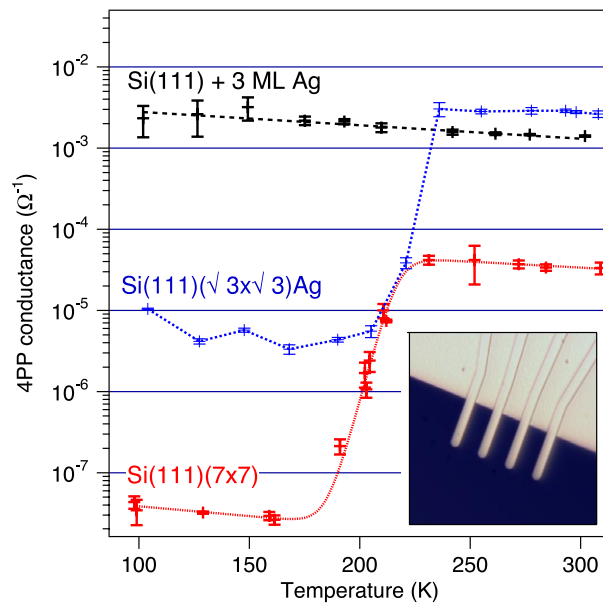


Figure 1. Experimental results for the clean Si(111)(7 × 7) surface, the Si(111)($\sqrt{3} \times \sqrt{3}$)Ag surface and the Si(111) substrate after the deposition of a nominal three-monolayer (ML) Ag film. The latter preparation results in a percolated network of Ag islands with a preferential thickness of 5 ML. A typical probe is shown in the inset.

accurate, but there are small deviations in the absolute value of the conductance and this is attributed to small variations in the deposition rate. For the Si(111)($\sqrt{3} \times \sqrt{3}$)Ag surface, the overall curve shape can be reliably repeated but, despite great care in the sample preparation, the transition temperature is found to only be repeatable to within ± 20 K, and the absolute conductance also shows small variations. From the work of other groups, most notably the work of Nakajima *et al* [26], Crain *et al* [23] and Matsuda *et al* [24], this can be explained as being due to the coverage dependence of the surface conductance and phase transition temperature.

In order to interpret the measured data correctly, it is first necessary to understand the temperature-dependent behaviour of the substrate and the clean surface. As shown in previous work [5], the strong transition observed for the clean surface can be attributed to switching between surface sensitivity (at low temperatures) and bulk sensitivity (at higher temperatures). This has been demonstrated empirically, by changing the bulk doping, and by means of a numerical finite-element method in which the behaviour of the bulk and space charge layer are considered. The results of this model, along with the measured data, are shown in figure 2(a). The model shows relatively good agreement with the measurements except at low temperatures. Here the model shows an ever-decreasing conductance, whereas the measurements show a low-temperature limit of $\approx 10^{-8} \Omega^{-1}$. Since the surface contribution to the conductivity is not included in the model, it can be inferred that the measurement is surface dominated in this temperature region.

Whilst it is tempting to say that the strong transition observed in the conductivity of the Si(111)($\sqrt{3} \times \sqrt{3}$)Ag sample may be explained similarly, this is in fact not the case. By applying the same numerical method to this sample, it becomes clear that the model and the measurements do not show any agreement (as shown in figure 2(b)). The measured conductance is significantly higher than the model across most of the measured temperature range. Again, the model does not include the surface contribution to the conductance. Therefore, this apparent

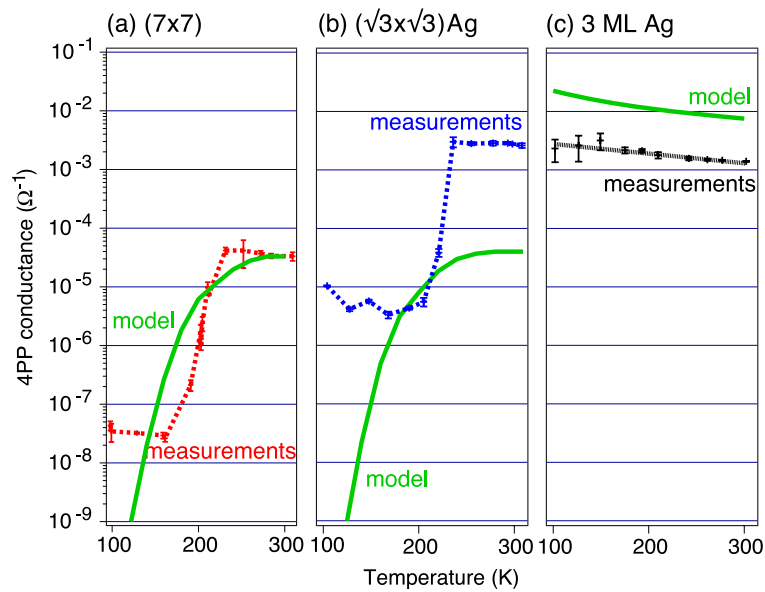


Figure 2. Experimental results from figure 1, together with simulations of the conductance. The solid lines represent a model calculation for the expected conductance of the bulk and space charge layer in (a) and (b) and for the expected conductance of a 3 ML Ag film with bulk properties in (c).

disagreement can be resolved by interpreting the measured conductance as being dominated by the surface conductance at all temperatures.

Modelling the influence of the space charge layer and bulk requires the pinning of the Fermi level at the surface (E_{sf}) to be known. For the Si(111)(7×7) surface this is generally accepted to be 0.65 eV above the valence band maximum [34]. However, for the Si(111)($\sqrt{3} \times \sqrt{3}$)Ag surface, the surface Fermi-level position has been a subject of some debate [21, 23, 26, 35]. Perhaps the reason for this is that the position of the surface state has been found to be strongly dependent on small deviations from a perfect 1 ML coverage [23]. Therefore, in our model, we use the mid-range estimate of $E_{sf} = 0.26$ eV from [23], thus the space charge layer is found to be a relatively weak hole-depletion layer at low temperatures and a weak hole-accumulation layer at room temperature. Since there is some uncertainty in the surface Fermi-level position, there is a corresponding uncertainty in the modelled conductivity. However, this uncertainty is too small to explain the failure of the model to reproduce the measured conductivity.

A similar interpretation can be made for the Ag film. In this case, the conductivity is much higher than that of the bulk and is therefore thought to dominate the measurement at all temperatures. The value of the conductance of this Ag film can be modelled by assuming that it exhibits the transport properties of bulk silver. This approach ignores all quantum size effects, defect scattering, and so forth, however it still provides a useful order-of-magnitude estimate. The result of this model is also shown in figure 2(c). Note that this model is quite different from those in figures 2(a) and (b), which give the conductance expected for the bulk and space charge layer. Here this contribution is ignored and the calculation represents only the properties of the thin film.

As expected for a model ignoring defects and boundaries, the simple model over-estimates the conductance of the film. However, the temperature-dependent behaviour of the conductance is reasonably well reproduced. Thus it can be inferred that the film behaves as a good metal

(i.e. it has a high conductivity which has a gentle negative gradient). In bulk silver, the temperature dependence of the conductance is dominated by electron–phonon interactions. Since the measurements performed on the thin film show a similar behaviour, it is reasonable to assume that the same mechanism is also dominant here. In principle, this allows the transport electron–phonon mass enhancement parameter (λ_{tr}) to be extracted from the four-point conductivity measurements but, since this is rather complex, it is not attempted here.

Again, the Si(111)($\sqrt{3} \times \sqrt{3}$)Ag sample can be considered. The room-temperature conductivity is of a similar magnitude to that of the thin Ag film in figure 2(c) and far higher than that expected for the bulk and space charge layer, thus it must be inferred that these measurements are surface dominated. At lower temperatures, the measured conductance is approximately three orders of magnitude less, but still several orders higher than the conductance of the bulk and space charge regions, thus it is also inferred that the measurements are surface dominated. Finally, it can be seen that the most plausible explanation for the observed transition in the measured conductance must be that it is due to a transition in the surface conductivity. A very likely explanation for this transition is the HCT-to-IET transition reported in the literature.

The microscopic origin of this phase transition is not known and recent experimental work even questions its existence. It is clear that our data supports the existence of a transition. An explanation of the transition’s driving mechanism is likely to come from theory, but even the most recent first-principles calculations are not in a position to describe the electronic structure of the surface very accurately [20], especially its semiconducting character. In any event, a symmetry-breaking phase transition would typically reduce the density of states at the Fermi level, and would therefore be expected to result in a significantly lower conductance in the low-temperature phase (see, for example, [1]).

In conclusion, the temperature-dependent conductivity of three contrasting surfaces has been measured. For clean Si(111)(7×7), the measured conductance shows a strong transition at about 200 K. This has been explained in previous work by the switching between surface- and bulk-dominated measurements [5]. For the Ag island film, the measured conductance is always surface dominated and the surface is found to be a good conductor with a temperature dependence comparable to that of bulk silver. The Si(111)($\sqrt{3} \times \sqrt{3}$)Ag measurements are also found to be surface dominated at all temperatures, and the absolute value of the conductance at room temperature is comparable to that of the Ag island film. However, at about 220 ± 20 K, the surface conductance undergoes a strong transition which is explained in terms of the geometry-altering phase transition reported elsewhere. The transition temperature is found to be dependent on the surface preparation which, after consideration of the surface electronic structure, is to be expected. Finally, in order to understand the temperature-dependent conductivity measurements on semiconducting substrates, and in order to disentangle the surface contribution to the measured conductance, a finite-element model of the bulk and space charge layer has been found to be invaluable.

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