Hindered electronic transport in two-dimensional metallic ErSi$_2$ nanoscale islands on Si(111): An STM study

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We have investigated by scanning tunneling microscopy (STM) discontinuous two-dimensional erbium silicide layers grown on the Si(111) surface. At low temperature (45 K), the characteristic spectral features of the islands are observed to shift in energy with decreasing tip-sample distance. This effect is observed for $n$- and $p$-type substrates with different doping levels, and for positive and negative sample biases. The analysis of the data suggests that the transport of charges parallel to the surface is the limiting process at low temperature.

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I. INTRODUCTION

The issue of charge transport at the surface of semiconductors has received some attention in the last few years. One question is to know whether surface states located in the band gap of the semiconductor (SC) can transport a current. They would be very interesting systems to study the fundamental mechanism of electrical transport in two dimensions since these states may be analysed in detail by a wealth of highly sensitive surface state techniques, including scanning tunneling microscopy (STM) and spectroscopy (STS). Measuring the surface conductivity is however a difficult issue, although significant progresses have been made recently (see, for instance, Refs. 2–4). In addition, several STM/STS studies performed at low temperature on clean semiconductor surfaces have revealed a variety of effects that have been ascribed to nonequilibrium or charging effects.5–10 Basically, when charges (electrons or holes) are injected by the STM tip into surface states located inside the bulk SC band gap, they generally have to overcome an energy barrier to be transferred directly to bulk states, and eventually to the sample contact. This local process can be hindered at low temperature, leading to local charge accumulation at the surface. Alternatively, charges can be transported away from the tunneling area by conduction along the surface. The efficiency of this channel in turn depends on the transport properties of the surface state bands. Various mechanisms have been proposed to explain the charging effects observed on semiconductor surfaces but, to our knowledge, no general agreement has been reached so far.

In this paper we report the results we have obtained on a system which differs somewhat from the clean or homogeneous SC surfaces considered above. It consists of disconnected islands of a metallic two-dimensional phase (ErSi$_2$, 2D silicide) grown on the Si(111) surface. The typical island size and/or separation is a few nanometers. Although they show spectroscopic features that are characteristic of the connected silicide layers$^{11,12}$—including standing wave patterns due to the lateral confinement of the surface electronic states$^{12}$—the position of these structures is found to change with the tunneling conditions for positive and negative sample biases. We have considered several classical mechanisms that could give rise to this phenomenon: tip-sample electrostatic interaction, bulk resistivity effect, and transport of charges in the interface region, both parallel and perpendicular to the surface. From an order of magnitude analysis of the data, we propose that the transport of charges parallel to the surface plane plays a significant role at low temperature.

II. EXPERIMENTAL DETAILS

From a technical point of view, we have used two different kind of Si(111) substrates. One was highly $n$ doped: dopant $B$, room-temperature resistivity $15–17$ m$\Omega$ cm, which corresponds to a doping level of typically$^{13}$ $4.0 \times 10^{18}$ cm$^{-3}$. The other one was moderately $n$ doped: dopant $P$, room-temperature resistivity: $0.8–1.0$ $\Omega$ cm, which corresponds to a doping level of typically$^{13}$ $5.5 \times 10^{15}$ cm$^{-3}$. The use of different type and level of doping is helpful in the discussion of the various mechanism of charge transfer in the sample. For a given position of the Fermi level in the SC gap at the surface, the doping type imposes the direction (upwards or downwards) of the band bending in the space charge layer, whereas the doping level determines the width of this depletion layer.$^{13}$ In our case, it is thought that the Fermi level is...
Confinement effects have been used to detect spectroscopic features both below and above the Fermi level of the silicide, thus allowing a study of the bias dependence of the observed phenomenon. The variable temperature STM setup and the spectroscopic imaging techniques we have used for these experiments have been described previously. Tunneling spectra are acquired at fixed tip-sample separation by interrupting the feedback loop and ramping the sample bias. These spectra are acquired at fixed tip-sample separation by interrupting the feedback loop and ramping the sample bias.

Local spectra can be taken at a given position on the surface (i.e., without scanning). Alternatively, we have performed “spectroscopic imaging” using the current imaging tunneling spectroscopy (CITS) method that essentially consists in measuring constant separation spectra at each point of a topographic image. The stabilization current and bias in this case are those of the topographic image. From this data set we can either extract local spectra or we can construct conductance images at a given bias, as illustrated in Fig. 2. Low-temperature experiments have been performed at typically 45 K.

Disconnected silicide islands are prepared by evaporating less than half a monolayer (ML)—typically 0.3 ML—of erbium on a clean Si(111)7×7 surface and annealing for 15 min at about 400 °C. This is the same procedure as the one we have used in our previous work to grow continuous layers of 2D silicide, except that we reduce the amount of deposited Er. Although we have not tried to determine a “percolation threshold” accurately, we have observed that when more than 0.5 ML of Er (nominal) are deposited connected layers generally form, whereas they are disconnected when the amount of deposited Er is below 0.5 ML using this preparation technique. The Si(111)7×7 surface was prepared by repeatedly flashing the substrate up to 1150 °C.

III. RESULTS

Topographical images of selected samples taken at about 50 K are shown in Fig. 1. Figures 1(a) and 1(c) are large scale images obtained on p- and n-type substrate, respectively. Portions of the surface of the substrate that remain uncovered appear in light grey. Islands of the 2D silicide show up as bright and flat areas [the amount of Er deposited was smaller in Fig. 1(c) than in Fig. 1(a)]. They coexist with small pieces of parasitic phases, some of them are indicated by arrows in Figs. 1(a) and 1(c). The size of the 2D silicide islands ranges from a few nanometers to 20–30 nm. Small scale images of the same samples as in Figs. 1(a) and 1(c) are shown in Figs. 1(b) and 1(d), respectively. The Si surface between the silicide islands appears as strongly disordered at high Er coverage [Fig. 1(b)]. At low coverage the quality of the surface reconstruction is better, although some disorder remain [circle in Fig. 1(d)]. In both cases dark spots are frequently seen at both polarities along the island edges.

When tunneling spectroscopy is performed on these disconnected silicide islands, it is found that the shape of the spectra depends on the tunneling conditions. One example is shown in Fig. 2(b), which displays three spectra taken at the centre of the triangular island of Fig. 2(a). This island was found on the same sample as the one shown in Figs. 1(a) and 1(b) (p-type sample) but at a different location. The tip-sample distance was set for each spectrum by changing the current, this varia-
observations of free-electron-like surface states and with decreasing sample bias, in agreement with our previous results.

The electronic structure is due to the measurement process itself. A shift of a characteristic surface electronic structure (the SSO) is observed at positive bias, but a similar effect is also found at negative bias. To establish this point we have used the confinement effect that gives rise to modulations of the otherwise smooth local density of states (LDOS) of the 2D silicide electronic structure. For a nanostructure with an approximately triangular shape like the one in Fig. 2(a), we observe in conductance ($dI/dV$) images a series of standing wave (SW) patterns that become more and more complex with decreasing sample bias, in agreement with our previous observations of free-electron-like surface states and with the actual downwards dispersion of the band. Some of them are shown in Figs. 2(c)–2(e). Without entering into details, these patterns reflect the modulus squared of the wave functions of the eigenmodes of the triangle. The corresponding eigenenergies show up as successive minima and maxima in the spectra taken at the center of the triangle [Fig. 2(b)]. Specifically, the structure labeled A that gives rise to a minimum in the spectra of Fig. 2(b) corresponds to a SW pattern with a minimum at the centre and four minima along the sides of the triangle in conductance images [Figs. 2(c) and 2(d)]. This structure is shown to shift with increasing stabilization current both in the spectra of Fig. 2(b) and in the conductance images of Figs. 2(c) and 2(d). The conductance image of Fig. 2(e), taken at the same energy as the one of Fig. 2(d) but with a larger stabilization current [the same as in Fig. 2(c)] confirms the effect of increasing current on the SW patterns. The interesting point here is that the shift of the electronic features with increasing stabilisation current seems to be of the same order of magnitudes at both positive and negative biases [e.g., for structures A and B in Fig. 2(b)], and in both cases corresponds to an apparent increase (in absolute value) of the energies of the structures. Since the tip-island voltage drop should remain the same for any given structure irrespective of the set-point parameters, this result implies that part of the applied sample bias drops between the surface of the sample and the sample contact.

Figure 3 gives a more quantitative account of the effect observed on the disconnected silicide islands. In Fig. 3(a), we have plotted the evolution of the position (i.e., the apparent bias) of the various structures that show up in spectra taken at the centre of the triangle of Fig. 2(a) as a function of
the injected current. The injected current is the tunneling current measured at the voltage corresponding to a given spectroscopic feature. In other words this is the current injected in the island when the Fermi level of the tip is aligned with the related spectroscopic structure (it is therefore different from the stabilization current defined in Sec. II). The apparent biases (positions) of the structures were obtained from difference spectra, where the average spectrum of the whole island is subtracted from the spectrum at the center [this procedure is used to remove the background in raw spectra such as those of Fig. 2(b)]. We have used the injected current as a variable for the plot instead of the stabilisation current since it allows a direct comparison of data from spectra acquired using different set-point voltages (−1.5 and −2.5 V in this case). With this choice the points obtained from spectra taken using different Vset fall essentially on the same curve since the injected current is also a measure of the tip-surface distance. Hence the injected current for a given structure (that is, for a given tip-island bias) defines both the electrical and geometrical state of the system. One can again see that the shift of the various spectroscopic structures seems not to depend much on the sign of the bias (notice that in a first approach to the problem we only consider orders of magnitudes of the effects in the present paper). This remains true for nanostructures grown on the n-type substrate (not shown). In Fig. 3(b) we show the position of the SSO (which is more readily obtained than structures due to confinement effects, in particular it does not require a well-defined island shape) for a selection of the samples we have investigated (two different doping and two different coverage for each doping). The upper points in Fig. 3(b) (n-type No. 2 and p-type No. 2) come from samples with lower coverage than the two others [n-type No. 2 is from the sample of Figs. 1(c) and 1(d), p-type No. 1 is from the sample of Figs. 1(a) and 1(b)]. From these curves, it appears that the evolution of the position (apparent bias) of the SSO with injected current does not depend systematically on the nature (n or p) of the substrate since the data from the n-type sample (filled symbols) fall on both sides of the data from the highly doped p-type one (open symbols).

The reason for the variations of the SSO extrapolated at zero current from one sample to the other in Fig. 3(c) is not known at that time. It may be of intrinsic origin, or it may be related to different tip electronic or geometric structures since several different tips have been used for the experiments. As for a possible intrinsic origin, it might originate from a change in the filling of the band in the silicide island due to some charge transfer which could vary from sample to sample depending, for instance, on the coverage or on the density of defects at the surface (which also modify the band bending in the substrate). However, due to the relatively small width of the metallic (surface) silicide band (less than 2 eV), a shift of the Fermi level by 100 meV relative to this band would result in a huge accumulation of charges in the island, whereas simple considerations suggest that the band filling changes by about 1% (or less) due to the band bending only. We believe that the dispersion in the value of the SSO extrapolated at low current in Fig. 3(b) is essentially due to different tip structures. This is a well-known effect, and we have actually observed apparent changes in the position of the SSO of the same order of magnitude (=100 mV) on continuous samples depending on the tip condition (and sometimes no traces of the SSO at all). For the data reported here we have checked that the structure of the tip has not changed in the series of spectra. In this report we focus on the shift of the SSO with current, which is observed irrespective of the tip structure for disconnected islands.

Finally, a few other observations have been made. The first one is that this effect is absent in experiments performed at room temperature on both n- and p-type samples. The second point is that the evolution of the position of the SSO with injected current is only weakly dependent on the size of the considered island, since almost the same effect is obtained for neighboring islands whose area differ by a factor of typically 5 (notice that there is a systematic difference, but it is small compared to the overall shift and we shall not discuss it here). The third point is that no shift of the SSO with injected current could be detected on connected silicide layers at low temperature on both n and p substrates using several different tips. This indicates that the discontinuous nature of the sample is essential for the understanding of the effect we observe. A last observation is that in spectra recorded on the rather scarce ordered domains of the silicon surface close to the silicide islands we have also detected, for both n- and p-type samples, shifts in spectral features of the same order of magnitude as that found for the SSO. Figure 4(b) shows an example of such spectra. They correspond to averages of the whole silicon area surrounding the silicide islands displayed in Fig. 4(a). Three features, which could be adsorbed to adatoms (A and B) and restatoms (C), are observed to shift in energy (at both polarities) when increasing the stabilization current from 0.2 to 1 nA. The shifts of these features are comparable to the one observed (and measured with exactly the same tip) on the SSO of the silicide islands as shown in Fig. 4(c). Shifts of spectroscopic features with current could also be detected on disordered areas of the silicon surface surrounding the silicide islands [see, e.g., Fig. 1(b)], but due to disorder it is more difficult to determine the atomic origin of these structures.

To summarize our observations, we have observed at low temperature a variation of the position of the spectroscopic features of disconnected silicide islands as a function of the injected current. It indicates that only part of the applied bias drops between the tip and the surface. This effect does not seem to depend much on the type (p+ or n) of the substrate, and it appears both at positive and negative bias with similar magnitude. It is also observed on the bare silicon surface surrounding the silicide islands. Finally, it changes only slightly with the island size but it is absent on connected layers. In the next paragraphs we discuss the possible origin of this phenomenon and propose an interpretation in terms of transport parallel to the surface.

IV. DISCUSSION

Several well-known mechanisms should be considered to explain the shift of the spectroscopic features with decreasing tip-sample distance. In the following paragraphs we discuss the electrostatic tip-surface interaction, the spreading
resistance effect and the charge transfer across the space charge layer. Finally we examine the effect of the hindered transport of carriers parallel to the surface plane.

We begin the discussion by considering the so-called “tip induced band bending” (TIBB) effect. This is a purely electrostatic effect (that is, no electron transport is involved) that originates from the penetration of the electric field produced by the tip in the semiconductor. As a result, part of the sample voltage drops inside the substrate in the subsurface region (therefore modifying the space charge layer) and the actual tip-surface voltage is lower than the applied bias. This causes an apparent increase (in absolute value) of the energies of the spectroscopic structures of the surface which is qualitatively similar to the phenomenon we observe. We think however that this is not the main reason for the shift reported here. The tip induced band bending has been analyzed quantitatively for semiconductor surfaces that do not support surface states. It is found to depend strongly on the doping level, and it should be much smaller for our highly p-doped samples than for the lightly n-doped sample, whereas we observe a similar behavior on both substrates. Moreover, the experimental variation of the peak positions with the tip sample distance is much larger than expected for the TIBB [from I(z) measurements, d changes at most by 1.5 Å for the range of tunneling currents reported here]. A simple 1D model indeed shows that the influence of the TIBB should be quite small for the highly doped sample in the voltage and distance range considered here (if one takes into account the actual 3D geometry of the tip, the effect becomes even weaker). Notice that the large shift we observe for the SSO (and other spectroscopic features) on the silicide islands cannot, in our opinion, be ascribed to the variation with distance of the overlap of the tip-surface wave functions or to the so-called Stark shift, since this effect should also be observed on connected layers at low temperature or on disconnected islands at RT in a similar range of set-point current and voltages. We therefore believe that the discrepancy between the expected effects of a possible tip induced band bending and our experimental results is large enough to consider that it plays only a minor role in our case. Another point to consider here is that both the Si(111)7 × 7 surface and the silicide layer have a significant density of states close to the Fermi level. As a result the Fermi level should be strongly pinned at the surface and virtually no tip induced band bending is expected. This has been shown previously for the Si(111)7 × 7 surface. Since no shift of the SSO was found on continuous layers, this should also be true for the 2D silicide. We therefore conclude that the tip induced band bending is not sufficient to explain our results. The same conclusion has been reached in Ref. 8 where a specific surface structure has been shown to be strongly dependent on the tip-sample distance.

Since electrostatic (or equilibrium) effects cannot account entirely for the observed shifts, we have to consider the transport of charges between the STM tip and the back contact of the sample. Electrons tunnel from (to) the tip into (out of) states of the silicide islands which are located inside the substrate band gap. They have to be transferred from (to) there to the bulk states near the surface and inside the bulk to the contact. Transport of carriers into the bulk might give rise to a potential drop due to the “spreading resistance” of the substrate, especially at low temperature (below ≈100 K) where the density of free carriers strongly decreases in moderately doped semiconductors. However, the resistivity increases only by a factor of 2 for our highly p-doped sample between 300 and 4 K, which suggests that the potential drop in the bulk should not change much between 300 and 45 K. Moreover it should remain much smaller than the one observed on the lightly doped n-type sample at any temperature. On the two types of substrates, similar shifts of the SSO are observed at low temperature but no effect is seen at RT. We can therefore discard this (bulk) spreading resistance effect as an explanation of the effect we observe at 45 K.

The transfer of the charges injected by the STM tip away from the tunneling point is a more serious issue. Due to
energy barriers at the interface or to a limited mobility of carriers in the surface region, the injected charges may not be easily evacuated out of an isolated silicide island. At the simplest level, the escape channel for the current from the metal island to bulk states may be modeled by a resistance $R$, whose value takes into account the hindered electronic motion (the value of $R$ may depend on the current). If $R$ is large enough (a fraction of a $\Omega$), a significant voltage drop $V'$ (of the order of 100 mV) will appear between the island and the bulk Si for tunneling currents in the 100 pA range. Therefore, the apparent bias of any electronic structure of the island will be shifted by $V'$, which is directly related to the injected current. This elementary resistive model would explain the strong dependence of the effect on the current. Actually, one should consider a parallel RC model as the most simple equivalent circuit of the island-bulk Si system, the capacitance $C$ being due, for instance, to the space charge layer below the island.\(^{13}\) The voltage drop $V'$ then leads to an excess of charges on the island (relative to the $R=0$ and $V'=0$ case). Alternatively, this can be viewed as an accumulation of injected charges on the island, that provides the voltage drop required to establish a current—equal to the injected current in the steady state regime—in the high resistance region between the island and bulk Si. The restricted transport of electrons\(^{5-9}\) and/or the accumulation of injected charges\(^{8,10}\) in the near surface region has been invoked in recent works to explain STM experiments performed on various semiconductor surfaces. To get insight on the origin of $R$, one should consider the different escape paths of the charges out of the island. Basically, the electrons (holes) injected at low energy (i.e., close to the Fermi level) by the tip can leave the silicide island by two ways: either by a transfer to bulk substrate states across the subsurface space charge layer (perpendicular to the surface) or by a migration along the surface (parallel to the surface plane). For the connected silicide layers we observe no change with current, consistent with an easy transport of charges in the metallic surface plane (the $R=0$ case). The break of this easy (short-circuit) path leads to the shifts observed for discontinuous films. In the next paragraphs, we discuss briefly some well-known mechanisms of electronic transport across the interface in an attempt to identify the effective charge transfer process at 45 K.

As shown by the observation of SW patterns, the charges injected by the tip are delocalized over the whole island. In the perpendicular transport mechanism, electrons and/or holes generally have to overcome the potential barrier created at the surface by the space charge layer. The problem shows strong similarities with transport phenomena in Schottky diodes,\(^{13,24}\) and in a first approach the discussion will be based on this analogy. In particular, we shall not assign any special role to the “primary” charge, the one injected by the STM tip at the energy of any given spectroscopic structure. Among other reasons, this is because the injected current originates from all the states located between this structure and the Fermi level. In the Schottky diode analogy, $V'$ plays the role of the diode bias, and $R$ and $C$ are the junction resistance and capacitance, both being bias dependent in general.\(^{13,24}\) The two main processes of charge transfer are then (thermal) excitation above the barrier and tunneling across the barrier. From the basic theory of thermoionic emission, the efficiency of the former process should depend markedly on the sign of the bias for a given doping, and on the type of doping—$n$ or $p$—for a given sign of the bias\(^3,24\) (rectifying effect of the Schottky diode). As for the tunneling process, it should depend strongly on the doping level of the substrate, which determines the barrier width.\(^3,24\) In principle, it should be much more important for our highly doped $p$-type samples than for our $n$-type samples. The observation of shifts of the same order of magnitude for a given current at positive and negative biases on both $p^+$ and $n$ substrates suggests that these two processes are not active in our case. It is difficult to go beyond these simple considerations since the problem is actually complex. Some information are missing, especially the actual value of the local barrier in the monolayer range.\(^{25}\) Moreover, strong deviations from the behaviour of planar Schottky diodes have been reported for nanoscale islands.\(^{26}\) Nevertheless, the small dependence of the shift on the island size, especially for the highly doped sample,\(^{28}\) is another indication that perpendicular transport may not be the dominant transfer process.

Since we have not observed the expected manifestations of a significant current flow across the interface, we are led to consider that the resistance $R$ is related to the limited transport of charges parallel to the surface at low temperature. This would be consistent with the weak dependence of the shift on the island size since the resistance would be primarily determined by the global environment of the island. Parallel to the surface, conduction can take place either in the surface plane or through the space charge layer.\(^2\) Depending on the case, this later contribution may be strongly reduced at low temperature.\(^2,4\) Anyway, it is not surprising that the heterogeneous nature of the surface layer hinders the motion of carriers parallel to the surface. As shown in Fig. 1, silicide islands are partially bordered by pits and are separated one from the other by disordered Si areas. Moreover, a direct measurement of the transport properties of the Si(111)\(7\times7\) surface indicates that its overall conductivity decreases with decreasing temperature.\(^3\) Owing to disorder and temperature effects we therefore expect the conductance parallel to the surface to be small at low temperature (45 K), which results in a large value of $R$. We tentatively ascribe the energy shift we observe at low temperature to this effect, although we acknowledge that the detailed mechanisms of charge migration along and perpendicular to the surface would need further investigations.

At that point it is interesting to contrast our conclusions with those obtained in Ref. 5, where it was reported that a circular (insulating, with a suggested large energy gap) trench on an otherwise ordered Si(111)\(7\times7\) surface induces a potential drop between the inner and the outer part of the structure at 300 K. To some extent some similarities exist. Cutting a low resistance conduction path [the metallic silicide layer here and the Si(111)\(7\times7\) in Ref. 5] generates an additional voltage drop between surface and bulk, which is of the order of a few 100 mV in both cases. The energy barrier in the subsurface region (related to the band bending) prevents an easy transfer of carriers from surface to bulk states. But there also significant differences, related to the
fact that we have studied a different system. We do not observe any voltage drop at 300 K and our data reveal a temperature effect in addition to a purely geometrical one. Furthermore in our case the transport perpendicular to the surface (across the subsurface barrier) seems to play a limited role in the observed voltage shift at low temperature whereas it looks important in Ref. 5. We can therefore directly observe the effect of a restricted surface mobility of carriers at low temperature in a disordered two dimensional medium. Moreover, the measurement technique we use is different from the one reported previously,\(^5\) which allows the investigation of the low-energy range of injected current. In the present case we are dealing with electron states located inside the bulk semiconductor gap at the surface. This prevents a direct escape of part of the injected current to the surface. This phenomenon using substrates with two different doping, conditions at low temperature. From a qualitative analysis of the various possible mechanisms being a priori different, their relative importance may change between 300 and 45 K.

V. CONCLUSION

Characteristic spectroscopic structures of disconnected silicide islands have been shown to change with tunneling conditions at low temperature. From a qualitative analysis of this phenomenon using substrates with two different doping, we propose that the evacuation of charges injected by the STM tip into the silicide islands is limited by the transport parallel to the surface at low temperature.

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