

STM investigation of the charge transport mechanisms to nanoscale metallic islands on a semiconductor substrate

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Scanning tunneling spectroscopy (STS) was performed at room temperature on disconnected two-dimensional nanoscale metallic islands made of erbium disilicide (ErSi_2) grown on Si(111). Our aim was to investigate how the charges injected by the STM tip were transferred from the metallic island to the semiconductor substrate, and how the charge transport mechanisms were reflected in the STS data. For that purpose, the relative importance of the two possible conduction paths, parallel or perpendicular to the surface, was modified by oxygen adsorption. The spectra of oxygen-dosed samples were found to change with setpoint current on p -type substrates, whereas no shift was observed for clean samples. Since oxygen exposure only affects the Si surface, this effect was interpreted as a change in the easy conduction path between the islands and the bulk substrate from parallel to perpendicular to the surface (i.e., through the metal-semiconductor interface). We propose and detail a method based on the analysis of STS spectra to determine the characteristics of the nanoscale metal-semiconductor contact. The results are in agreement with previous point contact experiments, which validates our analysis.

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I. INTRODUCTION

The transport of charges in the vicinity of clean semiconductor surfaces is an important issue in various fields ranging from fundamental to applied physics. It is obviously of primary importance for understanding the electrical properties of surfaces¹⁻³ as well as the behavior of nanoscale metal-semiconductor contacts.⁴⁻⁶ More generally, it is a main issue for the understanding of the electrical and electronic properties of nanoobjects supported on semiconductor surfaces. It also appears to be an important point for scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) studies of semiconductor surfaces. Indeed, nonequilibrium (or “charging”) effects have been found in recent STS/STS measurements on clean Si(111) and Ge(111) surfaces at low temperature.⁷⁻⁹ They have been attributed to a restricted transport of charges in the surface plane or between the surface and the bulk⁷⁻⁹. In this paper, we report an STS study of two-dimensional (2D) islands of nanometric size grown on a Si(111) 7×7 surface, focusing on the transport properties. The islands are made of one monolayer of erbium disilicide (ErSi_2), which is a 2D metal,^{10,11} so that charges can, in principle, be injected by the STM tip at any energy inside these objects. The question is to know by which mechanisms the charges injected locally (at the nm scale) at energies located within the substrate band gap can be evacuated away from the injection point. This point is also relevant for the STS studies of surface states in the gap of clean semiconductor surfaces.⁷⁻⁹ Two main mechanisms can be considered. The first one is the transport of charges parallel to the surface, either in the surface state band or in the space charge layer, which is related to the electrical properties of surfaces. The second one is the transport perpendicular to the surface, where the charges generally have to overcome an energy barrier due to the gap of the semiconductor and to the band bending in the space charge layer. In the case considered here of metallic islands on silicon, this perpendicular path

should have characteristics similar to those of nanoscale metal-semiconductor contacts. The electrical properties of nanoscale metal-semiconductor contacts performed by point-contact experiments on well-defined surfaces⁴⁻⁶ have revealed significant differences with the behavior of macroscopic Schottky diodes, although the expected rectifying characteristics is generally preserved.

In our previous paper, we have reported nonequilibrium effects on STS spectra recorded on nanoscale silicide islands at low temperature (45 K) for clean samples.¹² This effect has been ascribed to a limited transport of charges parallel to the surface, which, of course, means that the parallel channel is still easier than the perpendicular one. In order to get direct information on the role of the perpendicular transport in the charging effect in STS, we have exposed similar samples to molecular oxygen. Indeed, O_2 exposure in the few langmuir range is known to reduce drastically the parallel conductivity of the Si(111) 7×7 surface, probably by decreasing the surface state conductance.⁴ This would ultimately suppress the transport parallel to the surface, leaving the perpendicular channel as the dominant mechanism to evacuate charges. Compared to clean samples, we have actually observed significant changes in the STS spectra at high tunneling current on O_2 dosed samples which are consistent with this expected change in the transport mechanism at 300 K. Using specific spectroscopic features of the silicide islands, we have been able to perform a (semi)quantitative analysis of the transport of charges between the island and the bulk sample using a serial impedance model. The results are consistent with previous point-contact experiments.⁴⁻⁶ This shows that the characteristics of a nanoscale metal-semiconductor junction can be derived without making contact to the sample, on the basis of STS data only.

II. EXPERIMENTAL DETAILS

The experiments have been performed in a UHV system equipped with a homemade variable temperature STM.¹² For

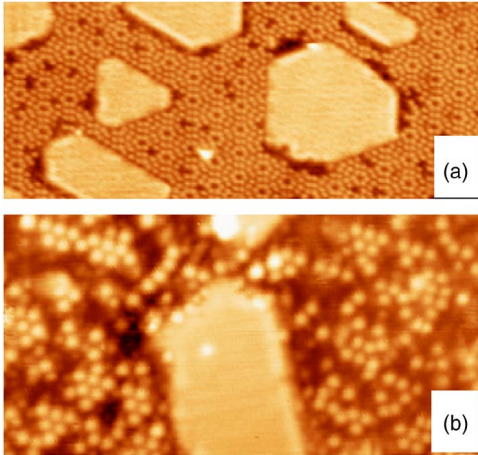


FIG. 1. (Color online) Constant current images of the samples. (a) Clean sample before exposure to molecular oxygen. Image size: $46 \times 23 \text{ nm}^2$ and sample bias: +1.0 V. (b) After exposure to 3 L O_2 at 300 K. Image size: $25 \times 13 \text{ nm}^2$ and sample bias: +1.0 V.

the present study, we have used *n*- and *p*-type Si substrates purchased from Siltronic (*p* type: B doped, 15–17 $\text{m}\Omega \text{ cm}$, *n* type: P doped, 1–5 $\text{m}\Omega \text{ cm}$). The clean samples have been prepared, as described in Ref. 12. They consist of disconnected silicide islands [smooth and light areas in Fig. 1(a)] separated by reconstructed substrate regions [mostly $\text{Si}(111)7 \times 7$]. Both the island size and the distance between islands are of the order of 10 nm.¹² These clean surfaces have been exposed to molecular oxygen, with typical doses of a few langmuirs (3–12 L) in the preparation chamber before being transferred to the STM chamber. As shown in Fig. 1(b), O_2 adsorption strongly modifies the substrate surface: the 7×7 reconstruction is essentially destroyed, although some adatom-related structures can still be identified, in agreement with previous reports.^{13–15} Detailed investigations reveal that the silicide islands are quite insensitive to O_2 adsorption in this exposure range, which will therefore mainly affect the transport of charges parallel to the surface.^{4,6}

III. RESULTS AND DISCUSSION

Current vs voltage $I(V_s)$ spectra (I is the tunneling current and V_s is the sample bias) taken at 300 K on a particular island of the O_2 -dosed sample of Fig. 1(b) are shown in Fig. 2(a), and their numerical derivative are displayed in Fig. 2(b). The substrate was *p* type. The shape of the spectra was virtually independent of the tip location inside a given island. In this series of spectra, the stabilization voltage V_{set} was set at +1.0 V, and the setpoint current I_{set} was varied between 0.1 and 5.0 nA. The spectra have been normalized to I_{set} for clarity. For clean samples at 300 K, series of spectra (not shown) normalized in this way fall one onto each other, as expected in tunneling spectroscopy for conductive samples. On the oxidized surfaces, the shape of the spectra change with injected current. This cannot be related simply to the change in tip-surface distance¹⁶ since no such effect is seen on the clean samples for similar variations. Indeed, it sug-

gests a change in the conduction mechanisms between surface and bulk after oxygen exposure. In the conductance spectra of Fig. 2(b), one notices a structure (peak) denoted as SSO. It is a characteristic spectroscopic feature of the *Er* disilicide layer which corresponds to the top of an almost occupied two-dimensional band.^{10,17} The apparent bias of the SSO at low I_{set} (+170 mV for $I_{\text{set}}=0.1 \text{ nA}$) corresponds to the value found at 300 K on clean samples, either for continuous or for discontinuous ErSi_2 layers, which confirms that the silicide islands are not perturbed by O_2 adsorption. With increasing I_{set} , this conductance peak shifts to higher apparent sample bias, as shown in Fig. 2(b) (hereafter the apparent bias of this peak is called V_{pos}). This shift demonstrates that part of the total bias applied to the sample (V_s) drops between the island and the bulk. Indeed, since the island is metallic with a high density of states close to the Fermi level (FL), the top of the almost occupied band will remain essentially fixed with respect to the FL of the island (within a few meV's which account for the accommodation of the extra charges required to support the voltage drops). Hence, the actual voltage drop between the tip and the island when tunneling into the top of the band remains close to $V_{\text{SSO}} = +170 \text{ mV}$ for any I_{set} , which means that the difference between the apparent bias of the SSO structure V_{pos} and V_{SSO} drops between the island and the bulk substrate. This configuration is depicted in Fig. 2(c), and it is basically similar to the nonequilibrium situation between surface and bulk invoked for some STM studies on semiconductor surfaces.^{7–9} Since we are in a steady-state regime, the voltage drop between the island and the bulk must have the value required to satisfy the continuity of the current to the island. The data of Fig. 2 show that a low resistance path between island and bulk has been suppressed by O_2 adsorption, and that the charges injected by the STM tip into the island can only be evacuated by a highly resistive channel for the oxidized surface. In a simple picture, the system can be modeled by the equivalent electrical circuit presented in Fig. 2(d), where Z_t is the (dc) tunneling impedance between the tip and the island and Z_s is a (dc) serial impedance between the island and bulk (V_t is the island voltage and V_s is the applied bias: when tunneling into the SSO, $V_s = V_{\text{pos}}$ and $V_t = V_{\text{SSO}}$). In the following, we shall see that it is possible to extract the current vs voltage characteristics of the serial impedance Z_s from our tunneling data, and thus to gain insight into the transport mechanisms between surface and bulk.

For positive bias, the characteristics of Z_s can be estimated from the shift of the SSO with increasing I_{set} . Let I_{pos} be the current measured at the apparent bias V_{pos} of the SSO for a given I_{set} . The characteristics of the serial impedance is obtained from $I_{\text{pos}}(V_{\text{pos}} - V_{\text{SSO}})$. This procedure refers to electrons injected in a rather wide energy range (200 meV above the FL), but similar results are obtained when electrons of lower energy are considered (see below). Additionally, an estimate of the conductance of the tunnel junction G_t may be deduced from the analysis of the SSO peak: $G_t = I_{\text{pos}}/V_{\text{SSO}}$. From the data of Fig. 2, we find that G_t changes by more than 2 orders of magnitude when I_{set} increases from 0.1 to 5.0 nA. Although this value of the tunnel conductance is strictly valid only for a special bias (V_{SSO}) between the tip and the island, it gives a correct order of magnitude of the

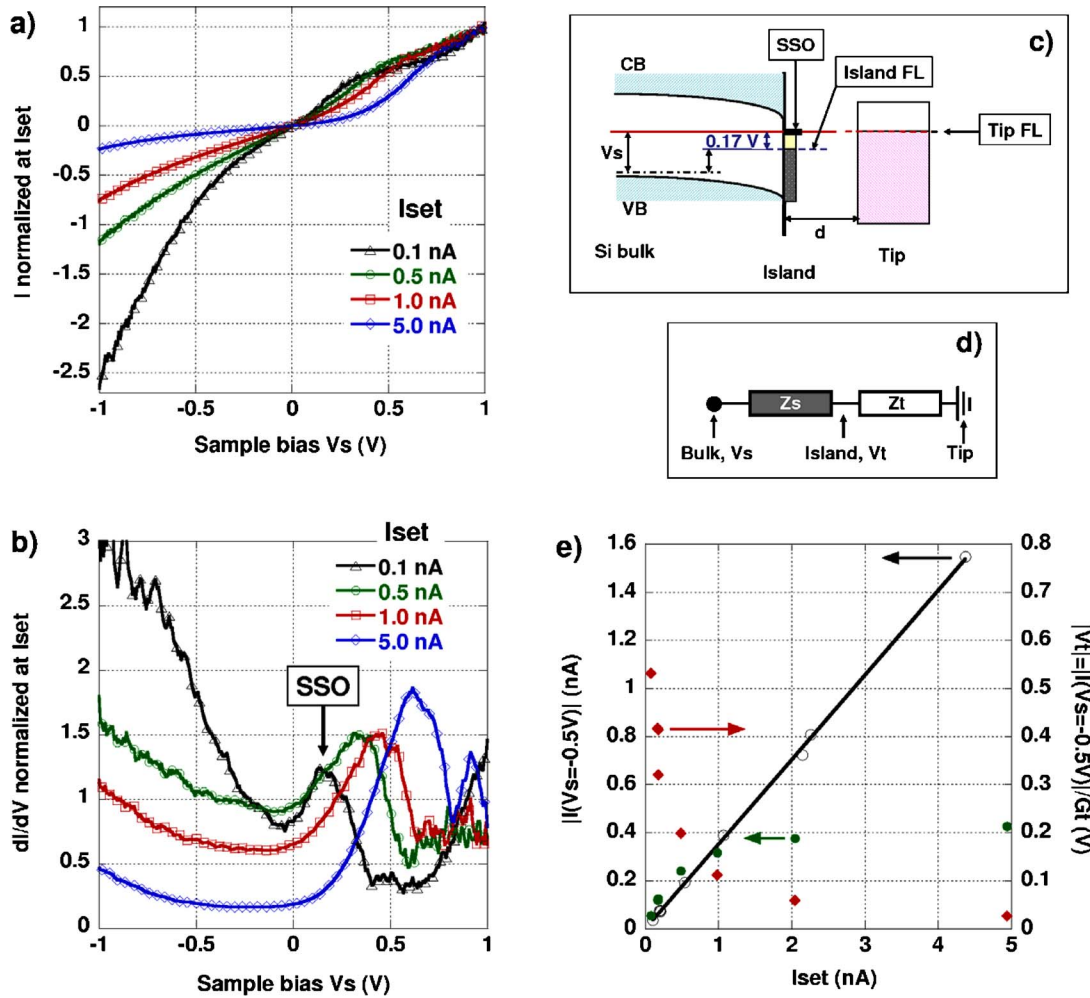


FIG. 2. (Color online) Spectra taken on a silicide island of a sample dosed with 3 L O₂ (*p* type substrate). (a) Current vs sample bias V_s spectra for different values of the setpoint current I_{set} (setpoint voltage: $V_{set}=+1.0$ V). The spectra have been normalized to I_{set} . (b) Numerical derivative of the curves of (a) (dI/dV spectra). The spectra have been normalized to I_{set} . SSO indicates the peak due to the surface state onset on the low I_{set} spectrum. (c) Schematic representation of the voltage drop between the tip and the island (0.17 V) and between the island and the bulk substrate when tunneling into the SSO ($V_s=V_{pos}$ in this case). The Fermi levels (FLs) of the different electrodes are indicated. (d) Electrical equivalent circuit of the system. Z_t represents the tunneling impedance between the tip and the island and Z_s is the serial impedance between the island and the bulk Si. (e) Filled circles: absolute value of the current measured for sample bias $V_s = -0.5$ V vs I_{set} for the spectra of (a). Open circles: same quantity for a clean sample (the line is a linear fit to the data). Diamonds: absolute value of the effective potential drop $|V_t|$ between tip and sample (for a sample bias of -0.5 V) estimated from the tunneling current (filled circles) divided by the tunnel conductance G_t (see text).

tunneling conductance for regular tips and for small voltages (from -0.5 to $+0.2$ V), as can be seen from the low I_{set} $I(V)$ and dI/dV curves of Fig. 2(a) which are similar to spectra taken on clean samples.

For negative bias, we consider the $I(V)$ curves such as those of Fig. 2(a). The ratio of the absolute value of the current at any negative bias to the value of the current at $V_{set}=+1.0$ V decreases while I_{set} increases. This indicates a rectifying behavior of the system, which can be quantified by plotting the actual current measured for a given applied bias $V_s (<0)$ as a function of I_{set} . The data corresponding to the spectra of Fig. 2(a) are shown in Fig. 2(e) for $V_s=-0.5$ V (filled circles): the current tends to saturate for large I_{set} for oxidized samples. This is in contrast to the linear variation observed on islands of clean samples (open circles), where

the shape of the spectra does not depend on I_{set} . Since the conductance of the tunnel junction increases with I_{set} , the saturation of the current for oxidized samples means that the actual bias between tip and island V_t decreases (in absolute value) for a given V_s . $|V_t|$ can be estimated using the values of G_t computed at the SSO by $|V_t|=|I|/G_t$, where I is the tunneling current. The result is shown (in the particular case $V_s=-0.5$ V) by the filled diamonds in Fig. 2(e) (right scale). As expected, the value of $|V_t|$ is close to 0.5 V for small I_{set} (small G_t) but decreases strongly with increasing I_{set} (increasing G_t) to reach values lower than 30 mV for $I_{set}=5.0$ nA. It means that the serial impedance limits the current for small tunneling impedance. Repeating this analysis for other values of V_s , we find that almost all the applied voltages V_s (more than 90% in the case of the spectra shown

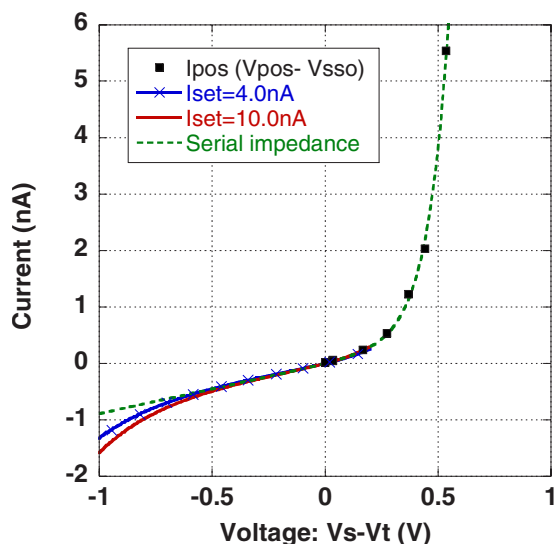


FIG. 3. (Color online) Current vs voltage characteristics of the serial impedance derived from our tunneling spectroscopy data. Filled squares are obtained from the shift of the SSO ($V_{\text{pos}} - V_{\text{sso}}$) with I_{pos} (see text). Continuous blue line with \times : raw $I(V_s)$ spectrum for $I_{\text{set}} = 4.0$ nA and continuous red line: raw $I(V_s)$ spectrum for $I_{\text{set}} = 10.0$ nA ($V_{\text{set}} = +1.0$ V for all I_{set}). The dashed green line is the characteristics of a diode with a resistor in parallel which represents the serial impedance.

here) drop in the serial impedance for small tunneling impedance in a range of applied biases V_s extending from large negative (-0.5 V) to small positive ($+0.2$ V) values. As a result, the large G_t (large I_{set}) $I(V_s)$ curves in this voltage range represent essentially the characteristics of the serial impedance.

As an example, we show in Fig. 3 the characteristics of the serial impedance deduced from the analysis of a series of spectra taken on another island of the same sample. The filled squares are obtained from the shift of the SSO with I_{pos} and the continuous lines are two $I(V_s)$ spectra taken at large I_{set} (4.0 and 10.0 nA for $V_{\text{set}} = +1.0$ V) and truncated at $V_s = +0.2$ V. In agreement with the previous considerations, the continuous lines almost coincide in an extended energy range close to and below 0 V. Moreover, they appear to follow the filled squares for small positive voltages. Since these two sets of data (continuous lines and squares) correspond to different energy ranges of the electrons injected by the STM tip into the island (between 0 and $+170$ meV above the island FL for the filled squares and less than 20 meV for the continuous lines), it seems to validate our procedure for estimating the serial impedance from the shift of the SSO. When the low G_t spectrum of this series ($V_{\text{set}} = +1.0$ V and $I_{\text{set}} = 0.1$ nA) is plotted on the same graph as the characteristics of the serial impedance (not shown), it appears that the less than 15% of the applied voltage V_s drops in Z_s for any current. The current at low G_t is limited by the tunneling junction and therefore the low I_{set} spectra resemble those of clean samples, as stated above. Finally, the $I(V)$ characteristics of the serial impedance have an asymmetric behavior and it can

be adjusted between -0.5 and $+0.5$ V by a formula such as $I = a[\exp(\alpha V) - 1] + bV$ (dotted line in Fig. 3) which describes a rectifying element (“diode”) in parallel with a resistor. The value of α is discussed below. The value of b (which describes a “leak” resistance) varies from one sample to the other, from 10^{-9} S to virtually 0 S. Its origin is unknown. It may be either intrinsic to the perpendicular transport mechanism or due to a very small residual conductance in the surface plane.

We have measured series of spectra at 300 K for several islands on three different p -type samples using different tips. The main features of the data of Figs. 2(a) and 2(b) have been observed in all cases after O_2 adsorption: a shift of the SSO structure with increasing setpoint current [with an almost exponential behavior for $I_{\text{pos}}(V_{\text{pos}} - V_{\text{sso}})$] and a clear tendency toward saturation of the current at negative biases for large I_{set} [leading to $I(V)$ spectra with a rectifying aspect]. Accordingly, the characteristics of the serial impedances deduced from these data have a shape similar to the one shown in Fig. 3 (with typical values of $\alpha \approx 9$ V^{-1}). The rectifying behavior of this curve is reminiscent of the characteristics of macroscopic^{18,19} or nanometric^{4,6} metal-semiconductor contacts. It indicates that transport perpendicular to the surface (from the silicide states to the bulk Si states) is the dominant mechanism at 300 K for evacuating the charges injected by the STM tip into the silicide islands for O_2 -dosed samples. This channel gives rise to a large impedance between the islands and the sample contact, which is shorted for the clean surface at room temperature. We believe that the easy (i.e., low resistance) conduction path on the clean sample corresponds to charge transport parallel to the surface, which is known to be strongly affected by the adsorption of oxygen.^{3,4} This is consistent with the removal of the dangling bonds of the substrate surface between islands observed in Fig. 1 and with our previous low-temperature experiments.¹²

When similar experiments are performed on a (highly doped) n -type substrate, only minor changes of the spectral shape with setpoint current are detected at 300 K after O_2 adsorption, although structural changes of the substrate surface are similar to those observed on the p -type samples. From our knowledge of the electronic structure of the interface, this is not unexpected even if the transport of charges takes place predominantly perpendicular to the surface. Actually, the Schottky barrier height of the 2D silicide on n -type samples is quite small, of the order of 100 meV,²⁰ which is close to the flatband condition. Moreover, the doping level of our n -type samples is quite high. Classical transport mechanisms invoked for metal-semiconductor interfaces (tunneling and thermoionic emission) (Refs. 18 and 19) can thus lead to a large current at small bias between the island and the bulk, and therefore to a serial impedance always smaller than the tunnel resistance, resulting in a negligible effect of the injected current on the shape of the $I(V)$ curves.

Going on with the analogy between metal-semiconductor interfaces and our island-substrate system, we find strong similarities between the curve of Fig. 3 and the characteristics found for point contacts of nanometric size.⁴⁻⁶ The current densities measured at a few hundred mV (or the zero bias conductance) are of the same order of magnitude—after suppressing the transport parallel to the surface by gas

adsorption⁴⁻⁶—and in any case much larger than the expected values based on a simple downscaling of macroscopic ErSi_{1.7}/Si(111) diodes.^{21,22} Moreover, the “ideality factor” of the diode—which is $40/\alpha$ at 300 K (Ref. 19)—is much larger than 1, resulting in a weak rectifying behavior (as compared to macroscopic diodes). Whatever the origin of the anomalous behavior of nanoscale diodes^{6,23} these similarities suggest that the procedure developed in connection with Fig. 3 can be efficient to estimate the characteristics of the contact between a fragile nanoscale object (which would be destroyed by point contact) and a substrate.

IV. CONCLUSION

To summarize, oxygen adsorption was found to change the easy conduction channel between nanoscale metallic islands and the semiconductor substrate from parallel to perpendicular. This leads to the observation of nonequilibrium phenomena in the tunneling spectra at 300 K. We have presented a (semi)quantitative way of analyzing the STS data which provide a reasonable estimate of the transport characteristics of the island to substrate contact.

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