Metal induced gap states on Pt-modified Ge(001) surfaces

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Abstract. Using scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) we have studied the electronic properties of a novel, planar, metal semiconductor contact. For this purpose we take advantage of the unique properties of the Pt-modified Ge(001) surface, which consist of coexisting metallic and semiconducting terraces. Spatially resolved STS measurements reveal that the higher lying metallic terraces induce electronic states in the band gap region of the lower lying semiconducting terraces.

The first high resolution experiments on the electronic structure of metal semiconductor contacts have been pursued for metal clusters on GaAs(110) [1]. As pointed out by Reusch et al [2] the depletion layer in the semiconductor component of these systems can only be probed indirectly. In this paper, the electronic structure of gold in contact with GaAs(110) in cross-section was studied. This planar geometry is obtained by in situ cleavage, offering access to the formerly hidden interface. It is, however, not completely clear whether the atomic structure at the interface is maintained in detail and, in addition, defects near the interface may be introduced throughout the cleaving process. Here, we describe a scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) study of the electronic properties of a planar metal semiconductor contact that does not suffer from the aforementioned drawbacks. For this purpose we take full advantage of the unique properties of a Pt-modified Ge(001) surface. It consists of two distinctly different terraces denoted by $\alpha$ and $\beta$. The $\alpha$-terraces behave as a p-type semiconductor with a band gap of about 0.4 eV and only contain Pt atoms in sub-surface positions, whereas the $\beta$-terraces are metallic and contain both Pt and Ge atoms [3]. The domain boundaries between the $\alpha$- and $\beta$-terraces are almost exclusively located at pre-existing steps. Our spatially resolved STS measurements reveal that the contribution to the tunneling current in the band gap region of
an $\alpha$-terrace in the proximity of a $\beta$-terrace is enhanced provided the latter constitutes the upper terrace. This remarkable, unanticipated observation is attributed to the coupling of metallic states of the upper lying $\beta$-terrace to virtual gap states on the lower lying $\alpha$-terrace.

Experiments were performed with a low temperature STM operating in ultrahigh vacuum (UHV). Ge(001) samples were cut from nominally flat 3 in. by 0.5 mm, single-side-polished n-type wafers. Samples were mounted on Mo holders and contact of the samples to any other metal during preparation or measurement was carefully avoided. The Ge(001) samples were cleaned by 800 eV Ar$^+$ ion sputtering and annealing at 1100($\pm$25) K. After several cleaning cycles the Ge(001) samples were atomically clean and exhibited a well ordered (2 $\times$ 1) and c(4 $\times$ 2) domain pattern [4].

Subsequently, 0.20–0.30 equivalent monolayers of Pt were deposited on to the surface at room temperature. Pt was evaporated by resistively heating a W wire wrapped with high purity Pt (99.995%). After Pt-deposition the sample was annealed at 1050($\pm$25) K for 10 min and then cooled down to room temperature before being placed into the STM for observation.

After deposition of Pt and subsequent annealing above 1000 K, both $\alpha$- and $\beta$-terraces are formed on the Ge(001) surface. The $\alpha$-terraces resemble the normal dimer reconstructed Ge(001) terraces rather well. The only clear difference is the relatively high amount of missing dimer defects. Most of these missing dimer defects can be identified as so called 2 + 1 missing dimer defects (two missing dimers followed by a normal dimer and a missing dimer defect). It is believed that this kind of defect is induced by the presence of a metal atom, such as for instance a Ni, Ag, Cu, Co or Pt atom, sitting in a subsurface position [5]. In figure 1(a), an STM image of an $\alpha$-terrace is displayed. $I(V)$ spectra recorded on these terraces reveal that they have a clear p-type semiconductor character at 77 K (figure 2(a)). This observation is consistent with data in the literature showing that Pt acts as an acceptor in a Ge crystal, thus leading to a p-type semiconductor [6].

The $\beta$-terraces are comprised of dimer rows too and they show improved ordering when compared to the $\alpha$-terraces. A closer inspection of the STM images reveals that they consist of an almost perfectly ordered array of two types of dimers, probably normal Ge–Ge dimers and mixed Pt–Ge dimers (for details see [3]). Another eye-catching difference is the presence of missing dimer defect chains that are mostly aligned along (310) directions (see figure 1(b)). STS measurements of these $\beta$-terraces show that these terraces are metallic at 77 K (see figure 2(b)). It is noted that Pt-nanowires are found exclusively on $\beta$-terraces. The Pt nanowires are found in patches as well as in isolation. These Pt nanowires have a cross-section of only

Figure 1. (a) STM images of an $\alpha$-terrace. (b) STM images of a $\beta$-terrace. The sample bias is –1 V and the tunneling current is 0.46 nA.
Figure 2. (a) log $I(V)$ curves as a function of the sample bias, measured at 77 K on two different and mesoscopically separated $\alpha$-terraces, far away from step edges. The letters C, V, and D refer to the valence band, conduction band and dopant induced components to the current. The arrows in the figure indicate the transition between the dopant induced current region and the conduction band induced current region. (b) The $\frac{dI}{dV}$ curve of $\alpha$- and $\beta$-terraces recorded at 77 K.

one atom, are kinkless, literally defect free and hundreds of nanometres long [7]–[9]. At low Pt-coverage, the vast majority of the surface consists of $\alpha$-terraces. However, if a certain threshold Pt-coverage is (locally) surpassed an $\alpha$-terrace converts into a $\beta$-terrace. Further increase of the Pt-coverage leads to the formation of extended Pt nanowire patches on top of the latter terrace. Both of the $I(V)$ curves shown in figure 2(a) have inflection points related to the dopant (D) and conduction band (C) induced components of the tunneling current. The difference in the dopant induced component of the $I(V)$ curves reveal that the relative Pt-dopant concentration of an $\alpha$-terrace differs from one $\alpha$-terrace to another [10]. However, due to the fact that the probability for tunneling into empty conduction band states declines steeply the location of the inflection points remains approximately constant. Figures 3(a) and 5(a) show three-dimensional (3D)-STM images of the topography of $\alpha$- and $\beta$-terraces in the vicinity of a step separating the two kinds of terraces. Note that two different step configurations are possible, namely a type-I step where the upper terrace is a $\beta$-terrace and a type-II step, when the upper terrace is an $\alpha$-terrace. The two steps show different features as will become clear later.

First, we will concentrate on the electronic properties in the close vicinity of a type-I step. These electronic properties have been studied in detail at 77 K by recording $I(V)$ spectra as a function of the distance away from the step edge. Spectra have been recorded simultaneously with the topography by opening the feedback loop at each point followed by swiftly ramping the voltage. As pointed out by Feenstra [11], the STM tip may alter the band bending. To check this possibility, careful measurements have been performed at different tip–sample separations, while keeping the tunneling parameters constant. We have not observed any evidence for a shift in the valence and conduction band edges. This clearly demonstrates that tip induced band bending does not occur in our system. This allows us to use the $\frac{dI}{dV}$ curves directly, without applying the normalization procedure suggested earlier by Feenstra.
Figure 3. (a) STM image of a type-I step (the upper terrace is a \( \beta \)-terrace). The sample bias is \(-1 \text{ V}\) and the tunneling current is 0.46 nA. (b) \( I(V) \) curves recorded in the proximity of the type-I step. The numbers on the right-hand side of the graph refer to distance measured between the point where the specific \( I(V) \) curve is recorded and the position of the step edge (here negative values refer to positions on the \( \alpha \)-terrace). The arrow in the figure indicates the inflection point of the graph, where dopant induced and conduction band regions separate (see text and figure 2(a)).

Figure 3(b) shows \( I(V) \) curves, measured in the close proximity of a type-I step as displayed in figure 3(a). Each curve has been averaged over at least 40 individual \( I(V) \) curves measured in a box with dimensions of 1 nm \( \times \) 4 nm (perpendicular and parallel to the atomic step, respectively). The valence band edges of all the \( I(V) \) curves measured on \( \alpha \)-terraces of type-I are pinned at the Fermi level. This indicates that the presence of a metallic \( \beta \)-terrace does not alter the band bending of a semiconductor \( \alpha \)-terrace [12].

The \( I(V) \) curves measured on the terraces near a type-I step (figure 3), show a gradual transition from the metallic \( \beta \)-terrace to the semiconductor \( \alpha \)-terrace. The conductance at the \( \alpha \)-terrace at moderately positive bias voltages (\( \sim 0.1–0.4 \text{ V} \)) depends strongly (note the logarithmic scale in figure 3(b)) on the position. On the \( \alpha \)-terrace side of the type-I step, the conductance and thus the density of states (DOSs) within the band gap on the \( \alpha \)-terrace is enhanced towards the boundary. This rather drastic increase of the current cannot be explained by an increase of the Pt-dopant concentration towards the step, since the \( I(V) \) curves do not exhibit an inflection point indicative of a transition from a dopant induced current to a conduction band induced one (cf figure 2). Therefore, the increase of the current is attributed to the development of virtual gap states originating from the \( \alpha \)-terrace. Note that when a semiconductor is in contact with a metal, wave functions of the metal with appropriate energy and wave vector can couple to the virtual gap states of the semiconductor. The resulting state is called a metal induced gap state (MIGS) [13]–[15].

The nearly free electron model for a 1D periodic potential, \( V(x) = V \cos(k \cdot x) \), predicts the opening of an energy gap of width \(|V|\) at the edges of the Brillouin zone. The dispersion of the nearly parabolic energy bands is strongly modified in the proximity of the zone boundary. It is convenient to express this dispersion in terms of a momentum vector \( q \) measured relative to the edge of the Brillouin zone, i.e. \( q = k - \frac{\pi}{a} \). The dispersion relation of the states near the
boundary of the Brillouin zone is represented by,

\[ E = E_B + \frac{\hbar^2}{2m} (q)^2 \pm \sqrt{\left( 4 \left( \frac{\hbar^2}{2m} \right) \left( \frac{\pi}{a} \right)^2 \left( \frac{\hbar^2}{2m} \right) (q)^2 + |V|^2 \right)}, \]  

(1)

where \( E_B \approx \frac{E_V + E_C}{2} \) is the branching point and \( E_V \) and \( E_C \) are the valence and conduction band edges. The solutions of the Schrödinger equation in the forbidden zone, i.e. the virtual gap states, have imaginary wave vectors and hence decay exponentially into the material [16]. For convenience we introduce \( q = i\tilde{q} \), where \( \tilde{q} \) is real. Equation (1) can be rewritten into,

\[ E = E_B - \frac{\hbar^2}{2m} (\tilde{q})^2 \pm |V| \sqrt{\left( 1 - 4 \left( \frac{\hbar^2}{2m} \right) \left( \frac{\pi}{a} \right)^2 \left( \frac{\hbar^2}{2m} \right) (\tilde{q})^2 |V|^2 \right)}. \]  

(2)

Because the energy, \( E \), must be real we deduce from equation (2) that,

\[ \tilde{q} \leq \frac{ma|V|}{\hbar^2 \pi}. \]  

(3)

At the boundary, the states originating from the metal couple to the virtual gap states and leak into the semiconductor. The penetration depth of these states is limited by the wave vector of the gap states, \( \tilde{q} \). The screening effect of these states within the semiconductor depends strongly on the dielectric constant (\( \varepsilon_\alpha \)) of the semiconductor. The DOS of a MIGS is defined as [17]:

\[ \text{DOS} = \int_0^\infty \exp(-2 \cdot q \cdot x) \cdot \rho_m \cdot dx \approx \frac{\rho_m}{2 \cdot q \cdot \varepsilon_\alpha}, \]  

(4)

where \( \rho_m \) is the DOS of the metal. A minimum in the density of the MIGS gap occurs near the middle of the gap at the maximum of the wave vector \( q = ma|V|/\hbar^2 \pi \). The ratio DOS/\( \rho_m \) can be interpreted as a mean penetration depth of the MIGS into the semiconductor.

The differential conductance, dI/dV, is proportional to the DOS. Therefore the dI/dV curves extracted from the I(V) curves presented in figure 3(b) reveal the spatial variation of the DOS of the MIGS (figure 4(a)). The mean penetration depth, as depicted in figure 4(b), is extracted from the data presented in figure 4(a). As expected, a minimum in the decay length occurs in the middle of the energy gap. The minimum mean penetration depth is about 2 nm.

It is noted that for a type-II step the spectroscopic data on both terraces show no discernable dependence on the distance from the step. This is to be expected for the metallic \( \beta \)-terrace, in line with the data for a type-I step. However, on the \( \alpha \)-terrace the I(V) curves are within the error limits identical. The latter is probably best illustrated by comparing the relative currents at positions of 1 and 5 nm from the step at a bias voltage of 0.3 V. Where for a type-I configuration the current is not less than two orders of magnitude higher for the short distance from the step (cf figure 3(b)), whereas the currents are identical for a type-II step (see figure 5(b)). Apparently, this implies that the MIGS are absent in a type-II step. At first glance, this might seem to be contrary to expectations. However, this observation is an additional proof for the fact that the metal–semiconductor contact is planar. In the type-II step configuration the metallic states of the lower lying \( \beta \)-terrace couple to the underlying bulk of the neighboring \( \alpha \)-terrace.

In summary, we have performed STS-measurements on planar metal semiconductor junctions. This unique geometry is inherently present on a Pt-modified Ge(001) surface,
exhibiting two microscopically and electronically different terraces, denoted by $\alpha$ and $\beta$. STM and STS measurements at 77 K reveal that the $\alpha$-terrace behaves as a p-type semiconductor with a band gap of about 0.4 eV, whereas the $\beta$-terraces are metallic. The boundaries between these two different types of terraces are virtually always found at pre-existing steps. This planar structure makes this specific and rare system predestined for an investigation of the metal semiconductor contact which in this case is directly accessible to STS, without major intrusions into the system. The electronic transition from a lower lying $\beta$-terrace to an upper lying $\alpha$-terrace is rather abrupt, whereas a much more gradual transition is found for the reverse case. In the latter case (type-I), metallic states of the $\beta$-terrace decay via the virtual gap states of the $\alpha$-terrace, leading to the formation of MIGS.
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