Tunable control over InSb(110) surface conductance utilizing charged defects

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ABSTRACT

Individual impurity atoms are playing an increasingly important role in next-generation conventional and quantum devices. We use the tip of a scanning tunneling microscope to deposit individual adatoms on an InSb(110) surface and control their charge state. In the positive charge state, adatom-induced band bending ionizes residual donors and produces an accumulation region with high conductance. Tip-induced charge neutralization switches the local band bending to depletion, producing a pronounced suppression in the surface conductance. A competing rates model is used to qualitatively explain the tunability of this effect as a function of bias voltage, tunneling set current and photoillumination.
As electronic devices miniaturize to few nm dimensions, the influence of any individual dopant or defect more significantly affects the performance of the device. Nanoscale electronics, such as single atom transistors, have pushed towards ‘solotronics’, where control and manipulation of individual dopant and defect atoms in a material determines the device performance. STM studies have shown a variety of defect phenomena including tunable field control of dopants in III-V semiconductors and spatially resolved studies of carrier dynamics near individual impurities via surface photovoltage detection. Ionization features that accompany these individual defects have been seen in a variety of contexts including dopants in GaAs, C60, cobalt on graphene, iron on Bi₂Se₃ and vacancies in ZnO. Further, ionization effects due to non-equilibrium charging rates of the defect have been seen in silicon dangling bonds.

Here we report a field-induced ionization feature that reveals how individual adatoms can be used to tune the tunneling conductance of an InSb(110) surface by two orders of magnitude over relatively large areas. When the adatoms are in a positive charge state, adatom induced band bending leads to a high-conductance accumulation region that can extend for > 100 nm due to the very low binding energy of native donors in InSb. Under certain tunneling conditions, the adatom can be switched to a neutral state when the STM tip approaches it, leading to a low-conductance region appearing as a ‘crater’ feature in topographic STM images. The crater size and depth can be tuned with bias voltage, set current, and illumination. These studies provide insight into how single atoms can be harnessed in future nanoscale opto-electronic devices.

Experiments were conducted in a Createc LT-STM at 5K in ultrahigh vacuum (< 10⁻¹⁰ mbar) using electrochemically etched Pt/Ir tips with an apex diameter <500nm. The InSb sample was a commercial bulk wafer, nominally undoped, but with n-type conductivity verified with Hall effect measurements. Typical donor species (e.g., S, Se, Te) in InSb are thought to occur
at a low concentration in the $10^{13-14}$ cm$^{-3}$ range, with a low, $\sim 0.7$ meV binding energy $^{18}$. The sample was cleaved at 100K in UHV, exposing the (110) surface, immediately before transfer into the STM. Tunneling spectroscopy was performed by adding a 10mV modulation to the sample bias. A lock-in detects the corresponding $dI/dV (V)$ signal, which is related to the local density of states (LDOS). To tune band bending via the surface photovoltage (SPV) effect $^{19}$, light from a home-built laser (1550nm, 100fs pulses) was aligned to a side viewport on the STM chamber. An average laser power of 1.5 mW was directed at glancing incidence onto the sample with no additional focusing. The illuminated area on the sample was relatively large ($\sim 0.5$ cm$^2$), so that careful alignment of laser and tip was not necessary.

Using SEMITIP by R.M. Feenstra $^{20}$, we performed simulations to model the local electrostatic potential at the surface due to the tip. Though the local potential depends on several tip parameters which are difficult to directly measure such as apex termination and work function, the simulations provide insight into the tip-induced band bending experienced by the nearby semiconductor surface. Based on the electron affinity of InSb and the estimated work function for the PtIr tips, we expect the flat band condition to be in the range $-0.2 \, \text{V} < V_{FB} < 0.4 \, \text{V}$ in our experiments.

Figure 1a shows an STM image of the clean InSb(110) surface under filled-state imaging conditions where the rows of Sb atoms are resolved $^{21}$, as are a few bright features which correspond to a low coverage of molecular adsorbates from the UHV chamber. Larger scale images of the surface (Fig. S1) show very few

**Figure 1. Adatom Deposition.** STM topographic images (a) before and (b) after a voltage pulse deposited an adatom to the InSb(110) surface (-0.5V, 0.22nA).
native defects such as surface and sub-surface dopants or atomic vacancies, which we attribute to the low residual doping level in our sample. During tip forming procedures (e.g. approach, voltage pulsing) that are typically used to sharpen STM tips, we were able to produce new point defects that we attribute to individual adatoms based on their small apparent size and reproducible appearance. Figure 1 shows the same area before and after a +8V pulse that dropped an adatom off the tip. We assign the dark spot to the atomic position, while the bright lobe to the side may reflect interaction with the neighboring surface Sb atoms, similar to a previous study of Fe/InSb(110)\textsuperscript{22}. Image contrast resolving both the In and Sb rows in Figure S2, shows the adatom in an interstitial location. The tip deposition process can be repeated multiple times, resulting in atoms dropped from the tip one by one. In prior work on GaAs, we found that the STM tip readily becomes terminated with the substrate material during the course of experiments and we could deposit Ga adatoms in a similar fashion.\textsuperscript{23} This suggests the adatom here is likely In or perhaps Sb. Similar effects to those described below were observed at step-edges and near larger nanoclusters that were occasionally deposited onto the surface during tip-forming (Fig. S8), suggesting this is a more general phenomenon that is not specific to the particular adatom species.

Figure 2 shows that the adatom images as a protrusion at negative bias (Fig.2a), and under positive bias conditions as a dark ‘crater’ feature (Fig 2b). Linecuts of the apparent topography as indicated in these images are shown in Figure 2c. At negative voltage, the apparent topography shows a gradual fall-off that extends for several nm away from the adatom site, much further than the atomic states associated with the adatom. This is commonly observed for charged species on III-V (110) surfaces\textsuperscript{24} and we attribute the change in topography to adatom-induced band bending (AIBB)\textsuperscript{25}. The tunneling probability depends on the total band bending (TBB) at the surface closest to the tip’s atomic termination. Consequently, changes in the local band bending will be
measured as changes in the apparent height of features in topography. In our system, there are several contributions to TBB from the tip and local environment:

\[ TBB = TIBB(V, z) + AIBB(q, \vec{r}) + \sum_{i=1}^{N} DIBB_i(q_i, \vec{r}_i) + SPV. \]

Here, tip induced band bending (TIBB) is a function of bias voltage \( V \) and tip height \( z \) which are varied in our experiments; adatom induced band bending (AIBB) is a function of the adatom charge state \( q \), and how far the adatom is from the tip, \( \vec{r} \); defect induced band bending (DIBB) represents the possible contributions from dopants in the local environment, and SPV is the surface photovoltage contribution if the sample is being illuminated. The separation of photo-excited carriers in local electrostatic fields always acts to decrease the magnitude of TBB, regardless of its sign.\(^{19}\)

**Figure 2. STM-induced charge switching** (a) Adatom under filled state imaging conditions appears as a protrusion (-0.5V, 0.22nA). (b) The same adatom under empty state imaging conditions appears as a ‘crater’ (+0.5V, 0.22nA). (c) Topographic linecuts across the adatom in panel a (orange) and panel b (green). In (a) increased accumulation due to AIBB<0 produces the gradual, nm-scale fall off in apparent height, while in (b), the abrupt switch to depletion conditions when AIBB = 0 suppresses the surface conductance by greater than 10x, resulting in an apparent depth of -1.5Å. (d) Tunneling diagrams for panels a and b that show increased accumulation due to AIBB < 0 (left) and an increased depletion region when AIBB = 0 (right).

The tunneling diagrams in Fig. 2d describe how the image contrast in Figs. 2a,b reflects the adatom charge state. Under the conditions in Fig. 2a, we can neglect the last two terms in Eq. 1, and we expect \( TBB < 0 \). Downward band bending causes an accumulation of conduction electrons under the tip. This accumulation region moves in concert with the tip, and while tunneling of these electrons into the tip’s empty states determines the absolute tip-sample distance,
it is largely invisible in the experimental images. The bright contrast near the adatom is consistent with a positive adatom charge state; downwards $AIBB < 0$ in our $n$-type sample increases accumulation near the adatom (orange shading in Fig. 2d) and the tip moves further from the surface in the constant-current image. The gradual fall-off in Fig. 2c (orange curve) follows a screened Coulomb potential $^{17}$, with a screening length of $\sim 3.5$ nm which also depends on accumulation due to TIBB (c.f., Fig. S3).

The crater feature at positive voltage (Fig. 2b), shows an abrupt change in apparent height of 150 pm, indicating $>10x$ reduction in tunneling conductance. The Sb rows are observed within the crater feature and appear continuous with the rows outside of the crater, indicating this is an electronic effect rather than a true topographic feature. The bottom of the crater is relatively flat (Fig. 2c, green curve), and there is no longer-range fall off in apparent height near the adatom position, suggesting that the adatom is not charged when the tip is inside the radius of the crater.

Under the conditions of Fig. 2b, TIBB $>0$ and AIBB switches from negative to zero as the tip approaches the adatom (green curves in Fig. 2d). The abrupt increase in TBB when $AIBB \rightarrow 0$ leads to an increased depletion region near the tip, and electrons must tunnel through a wider depletion barrier from the tip to the InSb conduction band. Consequently, the tip must now get significantly closer to the surface to maintain a constant current, accounting for the apparent depth of the crater feature.

The abrupt change in charge state as the tip approaches the adatom is suggestive of a tip-induced ionization effect. Recently, disk- or ring-like features in STM studies in other III-V semiconductors have been attributed to the ionization of individual dopants at a threshold value of TIBB that brings a dopant charge transition level into resonance with the host conduction or
valence bands. The size and shape of these features depend on factors which affect TIBB, including bias voltage, set current and the tip apex structure.

In Fig. 3 we demonstrate a similar tunability of the crater feature, however an alternate ionization mechanism is necessary to consistently explain all the data. Compared to the crater under typical imaging conditions (Fig. 3a), we observed a significant reduction in size by three methods: (i) illuminating the sample with light (Fig. 3c), (ii) reducing the set tunneling current (Fig. 3d), and (iii) increasing the bias voltage (Fig. 3b). Under illumination, SPV counteracts TIBB, so that the tip must move closer to the adatom to achieve the same threshold value. Similarly, a reduced set current (Fig. 3d) moves the tip further from the surface and thus reduces TIBB, which could be compensated by the tip moving laterally closer to the adatom to produce the crater feature.

While both of these observations are qualitatively consistent with a resonance TIBB ionization effect, the sensitivity of the crater to such small changes in set current and the reduction of the crater size with higher positive voltage (Fig. 3b) suggests an alternative mechanism is needed. For tip-induced ionization due to resonance of a charge transition level, the reduction in
crater size from +0.5V to +0.9V would imply a threshold $TIBB < 0$ and a large flat band voltage $V_{FB} > +1V$. As $V$ is increased toward $V_{FB}$, $|TIBB|$ gets smaller, and the tip must get closer to achieve the threshold condition, consistent with Fig. 3b. However, since $TIBB(V)$ is a monotonic function, we would expect progressively larger craters at negative voltages, and the adatom should remain in the neutral state in STM images. This is in contradiction to the long-range AIBB-induced contrast in Fig. 2a, which suggests a positive adatom is imaged under these conditions, and we have never observed crater-like features in STM imaging at negative voltages.

Following an approach recently developed for dangling bonds in silicon$^{13,14,16}$, we propose a competing rate model that is qualitatively consistent with all of our observations. In this model, ionization of a localized defect occurs due to a competition between the emptying rate to the bulk ($\Gamma_e$) and the filling rate from the tip ($\Gamma_f$). Here, TIBB does not ionize the adatom by bringing a charge transition level into resonance with the host bands, but rather TIBB can significantly influence $\Gamma_e$ by bringing the system into a double-barrier configuration, resembling a nanoscopic quantum dot coupled to two leads$^{14}$. Once the defect state is filled by an electron from the tip tunneling through the vacuum barrier, it must escape into the bulk by tunneling through a depletion barrier, with a height and width that depends on TIBB. The time-averaged occupation of the state is related to the ratio, $\Gamma_f/\Gamma_e$. 
Figure 4 schematically illustrates how this model can explain the corresponding data in Figure 3. Because the adatom is positively charged in the absence of the tip, we infer that the (+/0) charge transition level lies above the sample Fermi level and conduction band edge, and does not directly shift due to TIBB. When $E_{F,\text{tip}}$ is brought above the (+/0) level, the state can be occupied by an electron tunneling from the tip. Under the tunneling conditions in Fig. 3a and schematically illustrated in Fig. 4a, TIBB > 0, and the (+/0) level becomes occupied roughly when $\Gamma_f > \Gamma_e$, which occurs when the tip is at the crater edge. As the tip is brought closer to the adatom, $\Gamma_f$ increases and the adatom remains in the neutral state. Illumination (Fig. 4c) decreases the magnitude of band bending, which reduces the width of the depletion region and increases $\Gamma_e$, but has no direct effect on $\Gamma_f$. The tip must therefore approach closer to the adatom to increase $\Gamma_f$, consistent with the reduced crater size in Fig. 3c. Reduction of set current (Figs. 3d, 4d) directly decreases $\Gamma_f$, so that the tip must move closer to the adatom to achieve the threshold condition. Higher positive voltage (Figs. 3b, 4b) affects both rates: $\Gamma_e$ decreases because of a wider depletion barrier, while $\Gamma_f$ decreases because tunneling electrons from the tip have a higher vacuum barrier (assuming the (+/0) level is fixed with respect to the vacuum level). The data in Fig. 3b are consistent with a net reduction in the filling rate at higher positive voltage: the tip must approach...
the adatom to increase $\Gamma_f$ and achieve the threshold condition, resulting in a smaller crater. The filling/emptying rates are difficult to directly estimate from our STM data because they are sensitive to the measurement conditions and can easily lie outside the limited instrumental bandwidth, but we note that ‘telegraph’ noise is observed in STM images at higher positive voltage, when the crater is small and we expect both $\Gamma_c$ and $\Gamma_f$ to be reduced (c.f. Fig. S6, S7). Similar behavior was observed for charging of Si dangling bonds\textsuperscript{13,15}, and these dynamics may similarly be resolved by developing pulsed methods.\textsuperscript{16,27}

To identify the adatom charge transition level responsible for the ionization crater, we compared tunneling spectroscopy data with the tip positioned on pristine InSb (Fig. 5, black) and the adatom (Fig. 5, red). On InSb, there is a minimum of the LDOS in the range $\pm 200$ mV that roughly reflects the InSb band gap of 235 meV. A sharp rise at $+200$ mV is attributed to the InSb conduction band, and a more gradual rise below $-200$ mV reflects the valence band. Tunneling spectroscopy on the adatom indicates enhanced conductance below $-400$ mV consistent with increased accumulation due to $AIBB < 0$, and a pronounced suppression of the conductance above $+200$ mV, consistent with tunneling through a depletion region when $AIBB = 0$. We interpret the small peak at $+220$ mV as the $(+/0)$ charge transition level.

**Figure 5.** Tunneling Spectroscopy. $dI/dV$ spectroscopy on (red) and off (black) adatom showing an increase in the LDOS (red arrow) at 250 mV attributed to the $(+/0)$ charge transition state of the adatom. Inset shows the positions where the point spectroscopy were taken. Tip stabilized at $V = -0.5V$, $I = 0.22nA$ prior to spectra collection.
Somewhat counterintuitively, the spatial extent of the crater feature sets a lower limit for the length scale over which the adatoms influence the tunneling conductivity of the InSb(110) surface. Because the crater corresponds to the region where $AIBB = 0$, the apparent height of the surface outside the crater must reflect $AIBB \neq 0$, or there would be no change in contrast. To estimate this limit, we show in Figure 6 a series of images as a function of voltage with several adatoms deposited from the tip. With decreasing voltage, the crater features eventually grow to exceed the entire scan area, indicating that individual adatoms can influence surface conduction over distances greater than 50 nm.

We attribute the additional suppression of conductance on the left in Fig. 6c to filling from a point on the tip distinct from the tunneling apex (Fig. 6d). Although these points are further from the surface and have a wider vacuum barrier than the tunneling apex,

**Figure 6. Crater expansion.** (a) craters localized to their adatom. (b) With a modest change of bias (-50mV), craters expand and overlap. (c) further change (-50mV) shows more overlap and development of auxiliary crater. (d) filling point on the tip to the adatom need not be the tunneling point. Structure of the tip apex would allow for $AIBB$ to be modulated when the tip is far from the adatom.
they can be closer to the adatom and have a higher filling rate. This behavior further distinguishes ionization in the competing rates model $^{14–16,27}$ from the resonant TIBB models $^{6,8,26}$.

We present additional observations and TIBB simulations in support of the competing rates model in the Supporting Information, but we conclude that the remarkable spatial extent of the adatom-tunable conductance stems from the low binding energy ($\sim 0.7$ meV) of the residual donors in the undoped InSb crystal $^{18}$. This ionization energy is comparable to $k_B T \sim 0.4 \text{ meV}$ at 5K, which suggests that a sizeable fraction of the donors can be readily ionized thermally or by the electrostatic potentials of individual atoms. Indeed, for a $+e$ point charge, the Coulomb potential falls below 1 meV, $\sim 200$ nm away, assuming an effective static dielectric constant of $\varepsilon/2=8.4$ for the InSb/vacuum interface. This sensitivity distinguishes the ionization effect observed here from previous studies, and suggests that undoped semiconductors with a low concentration of very shallow dopants may be well suited for future solotronic devices.

ASSOCIATED CONTENT

**Supporting Information.** Additional experimental data and discussion are presented in the supporting information.

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**ABBREVIATIONS**

TIBB, tip induced band bending; TBB total band bending; AIBB, adatom-induced band bending; LDOS, local density of states; STM, scanning tunneling microscopy

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