Scanning Tunneling Spectroscopy on InAs-GaSb Esaki Diode Nanowire Devices during Operation

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In this supporting information we present in more detail: the technique used when mapping the surface potential of the investigated nanowires (NW) (1), the calculations of the GaSb and InAs bandgap (2), the normalization and evaluation of the tunneling spectra (3), the calculations of the surface band bending (4), the evaluations of the bandgap along the nanowires (5), the simulation made using COMSOL Multiphysics (6), and finally we discuss nanowire surface cleaning (7).

1. Mapping the nanowire potential

Figure S1. The technique used to determine the position of the bandgap along the nanowire. (a) STM image of the nanowire showing the thicker GaSb part (bottom) and the thinner InAs part (top). (b) The bandgap is here defined as the bias range where the normalized dI/dV signal is below a certain sensitivity threshold. This is done for all 250 spectra recorded in (a), and the energy position of the middle of the bandgap is plotted in color-scale over the position of the recorded spectra in (c).
In Fig. S1 the process of determining the position of the bandgap is described. 250 STS spectra in a 10 x 25 matrix are recorded over a 50 x 500 nm² area, Fig. 1(a). Each d/dV - V spectrum is normalized to the broadened I – V spectrum recorded simultaneously, Fig. 1(b), and the bandgap is here simply defined as the bias range where the (d/dV)/(I/V) signal is below a defined value. The center positions of the calculated bandgaps are then shown as a function of their position on the nanowire, Fig. 1(c).

2. Calculating the surface bandgap at the GaSb and InAs segments

The 10 (d/dV)/(I/V) spectra from each row in Fig. S1(a) were averaged and the resulting 25 spectra was then evaluated as described by ref 1 to determine the valence band (VB) and conduction band (CB) onset. Fig. S2(a) shows the averaged spectra from a row on the GaSb part of the nanowire and the functions used to calculate the band onsets. Fig. S2(c) shows the same but for InAs. In Fig. S2(b) the bandgap along the nanowire surface is plotted and a clear change is observed as the nanowire composition changes from GaSb to InAs between 200 and 250 nm. To calculate the bandgap for the GaSb part of the nanowire the values between 0 and 200 nm was averaged and to calculate the bandgap for the InAs part the values between 250 and 500 nm were averaged, omitting the transition region in between. The bandgap for the GaSb part was 0.39 ± 0.03 eV and for the InAs part 0.20 ± 0.05 eV.

Figure S2. The evaluation of the band onsets. (a) The averaged (d/dV)/(I/V) spectrum at 80 nm showing the functions used to determine the valence band (VB) and conduction band (CB) onset, shown as black. (b) The bandgaps calculated along a 500 nm stretch along the nanowire over the GaSb-InAs heterojunction. A larger bandgap is observed at the GaSb part as compared to a smaller at the InAs part. At the transition between the GaSb and the InAs a widening of the bandgap is observed. (c) Same as (a) but at the InAs part of the nanowire.

3. Normalizing and evaluating d/dV-V spectra

Upon characterizing the nanowire surface by STS, we simultaneously acquire I-V and d/dV-V spectra. Corresponding data, averaged for the GaSb (green) and the InAs (magenta) part of the nanowire, are shown as I-V spectra in Fig. S3(a) and as d/dV-V spectra in Fig. S3(b). In order to obtain the local density of states, independent of the distance between sample and tip, we calculate the normalized differential conductivity (d/dV)/(I/V), as described in ref 2. Thereby the total conductance (I/V) needs to be broadened by convolution with an exponential profile in order to avoid diverging results in the bandgap region. A broadening width ΔV which is roughly half the size of the observed bandgap is used.
In Fig. S3 we compare normalized averaged spectra, using the Feenstra method, from the GaSb (green) and the InAs (magenta) segment, applying broadening widths of $\Delta V = 0.2$ V (Fig. S3c) and $\Delta V = 0.4$ V (Fig. S3d). Using $\Delta V < 0.2$ V results in a divergence of the $(dI/dV)/(I/V)$ at the band gap edges due to the faster decrease of the current compared to the differential conductance. In Fig. S3(e) the tunneling current as a function of the tip bias for two individual spectra from both the GaSb (green) and the InAs (magenta)
part of the nanowire is plotted in semilogarithmic scale. In a region around 0 V bias, the current reaches the noise level of the STM preamplifier \(I_T < 0.1\) pA.

### 4. Surface band-bending

Generally, the extension of surface band bending radially into the nanowire due to Fermi level pinning at the nanowire surface is given by

\[
\frac{4\pi\varepsilon_0\varepsilon\phi_0}{2\pi n} = \left(1 - \frac{d}{3R}\right)d^2
\]

as shown by ref \(^3\). Here \(\varepsilon_0\) is the permittivity of vacuum, \(\varepsilon\) is the dielectric constant of the semiconductor, \(\phi_0\) is the surface Fermi level pinning potential, \(n\) is the doping concentration, \(R\) is the radius of the nanowire, and \(d\) is the length of which the band bending extends into the nanowire. For our calculations \(\phi_0\) is half the value of the bandgap since we assume that the Fermi level is pinned mid gap at the surface and is at the valence or conduction band edge in the bulk due to the high doping of the semiconductors. We apply this model here for estimating band bending in the nanowire due to the surface layer which exhibits small band gaps centered around the Fermi level. For the InAs part of the nanowire with a radius of 17.5 nm, Fig. S4(a), the band bending extends less than 16 nm into the nanowire at doping concentrations above \(1 \times 10^{18}\) cm\(^{-3}\), Fig. S4(b). For the GaSb part the extension is less than 7 nm above a doping concentration of \(1 \times 10^{19}\) cm\(^{-3}\), Fig. S4(c).

![Figure S4](image)

**Figure S4.** (a) Schematic representation of the investigated area of the nanowire (not to scale) also showing the extent of the band bending. (b, c) The radial extension of the surface band bending (due to surface Fermi level pinning) into the nanowire as a function of doping for the InAs (b) and GaSb (c) part of the nanowire.

### 5. Bandgap evaluation

In Fig. S5 the method used to evaluate the bandgap along the nanowire with an applied bias is shown. The nanowire is divided into two halves and the spectra are divided into 25 rows. The average of the spectra from individual rows from the left side of the nanowire is shown in Fig. S5(a), right side in Fig. S5(c). Close to the conduction and valence band onset, the \((dI/dV)/(dI/dV)\) signal can be fitted by a linear slope, additionally considering the thermal broadening at room temperature, which can be extrapolated to determine the conduction and valence band edges, as described by ref \(^1\). This is shown as the black lines in the spectra in Fig. S5(a). Here only the seven rows around the InAs-GaSb interface are shown for easy comparison. The spectra recorded with the nanowire grounded \((V_{NW} = 0\) V\) are shown in blue, red for
Figure S5. The nanowire is divided into two halves lengthwise, with 2 x 25 STS spectra obtained in each half, indicated by red and green x (b). Seven rows of spectra positions over the InAs-GaSb transition in the nanowire interface are marked by black rectangles. The average of the STS spectra from the seven rows, from the left (a) and right half (c), shows the transition in bandgap. The blue spectra are recorded with the nanowire grounded, the red with $V_{NW} = -0.2$ V, and the green with $V_{NW} = 0.1$ V. The black lines in (a) show the fitted functions used to calculate the valence and conduction band edge, and in extension the bandgap.

$V_{NW} = -0.2$ V, and green for $V_{NW} = 0.1$ V. Here the shifts of the spectra for different $V_{NW}$ are also clearly seen. Comparing spectra taken at different $V_{NW}$ also shows the reproducibility of the measurements as well as comparing spectra from both sides of the nanowire. The difference between the third and fourth spectra (in ascending order) from the left, Fig. S5(a), and right side, Fig. S5(c), of the nanowire is explained by the structural radial inhomogeneity of the nanowire at the InAs-GaSb interface seen in Fig. S5(b).
6. Calculating the potential along the nanowire

The potential along the core of the nanowire for \( V_{NW} = -0.2, 0, \) and \( 0.1 \) V was simulated using the computer software COMSOL Multiphysics and the results are presented in Fig. 4 of the main article, in good agreement with the measured potential. A 2D representation of the nanowire was created with a 30 nm wide InAs part (n-doping of \( 1 \times 10^{18} \text{ cm}^{-3} \)) and a 50 nm wide GaSb part (p-doping of \( 1 \times 10^{19} \text{ cm}^{-3} \)). The ends of the nanowire were contacted with ohmic metal contacts and the sides were covered with a 1 nm thick surface oxide layer that had a bandgap of 3 eV. For the heterojunction between the InAs and the GaSb thermionic emission was chosen as the continuity model.

7. Nanowire device surface cleaning

There are many techniques used to produce clean surfaces for STM measurements. Sputtering and subsequent annealing is routinely used to produce atomically flat and ordered metal surfaces. The technique is however not suited for III-V semiconductor studies because of ion impurities introduced while sputtering. Chemical etching has also been implemented which indeed helps to reduce the surface oxide on semiconductor nanowires and to passivate nanowire surfaces, but it does not produce atomically clean surfaces.\(^4\)\(^-\)\(^5\) For nanowires grown with molecular beam epitaxy As capping and subsequent evaporation has been used to great success to protect nanowire surfaces during transport through air, followed by STM characterization of free laying, atomically clean nanowires.\(^6\)\(^-\)\(^7\) This technique is however not applicable for our studies since the nanowires are grown by metalorganic chemical vapor deposition and because it would be incompatible with the additional processing needed when making nanowire devices.

The technique used in the article, atomic H cleaning, has previously been shown to create atomically clean surfaces on free laying InAs nanowires,\(^8\) GaAs nanowires,\(^9\) and InP nanowires.\(^10\) Cleaning nanowires with processed contacts at both ends however introduced a new problem. At temperatures above 400 °C the nanowire device is destroyed and for atomic H cleaning high enough temperature is crucial for complete oxide removal. The other parameter to tune is the H pressure which is limited by how high pressures your system can handle. Increased pressure however only shortens the cleaning time but it does not allow for complete oxide removal if the temperature is not sufficiently high.

The underlying mechanisms for the device destruction have not been thoroughly investigated by the authors but we speculate that mechanical strain due to thermal expansion might be one contributing factor to the device breakdown.
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