Supplementary Figures:

**Supplementary Figure 1:** Raman shift of the GaAs $A_1$-TO and $E_1$-LO phonon as a function of the clamp displacement.
Supplementary Figure 2: PL spectra of a WZ GaAs nanowire under compressive stress during a loading-unloading cycle.
Supplementary Figure 3: Decomposition of the unit cell deformation into isotropic and deviatoric components.
Supplementary Figure 4: Example of fitting the PL lineshape.
Supplementary Tables:

<table>
<thead>
<tr>
<th>Deformation potentials</th>
<th>LDA</th>
<th>GW</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Xi_{d,h} - \Xi_{b,h}$</td>
<td>5.69 eV</td>
<td>5.16 eV</td>
</tr>
<tr>
<td>$\Xi_{d,a}$</td>
<td>19.1 eV</td>
<td>21.0 eV</td>
</tr>
<tr>
<td>$\Xi_{b,h} - D_1 - 2D_2$</td>
<td>-7.60 eV</td>
<td>-8.25 eV</td>
</tr>
<tr>
<td>$D_3$</td>
<td>7.57 eV</td>
<td>7.68 eV</td>
</tr>
</tbody>
</table>

**Supplementary Table 1**: Deformation potentials extracted by different ab-initio methods, i.e. the Local Density Approximation (LDA) and the GW method.³
Supplementary Table 2: Stiffness tensor elements relevant for our strain experiment.\textsuperscript{1,2}

<table>
<thead>
<tr>
<th>Compliance Tensor Element</th>
<th>GaAs</th>
<th>Al\textsubscript{0.3}Ga\textsubscript{0.7}As</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{11}</td>
<td>145.3 GPa</td>
<td>145.4 GPa</td>
</tr>
<tr>
<td>C\textsubscript{12}</td>
<td>44.7 GPa</td>
<td>44.8 GPa</td>
</tr>
<tr>
<td>C\textsubscript{13}</td>
<td>35.6 GPa</td>
<td>35.7 GPa</td>
</tr>
</tbody>
</table>
Supplementary Notes:

**Supplementary Note 1: Buckling in Wurtzite GaAs Nanowires**

To be able to accurately model the effects of strain on the band structure and lattice dynamics, it is important to assess for which values of stress buckling occurs in the nanowires used. The maximum compressive strain applicable on the nanowire depends on the mechanical behavior of the nanowire at the two clamping regions. Depending on the clamping rigidity, we expect a critical buckling strain ranging between 1.2% and 2%. Most of the compressive stress range in which the direct-to-pseudodirect transition is observed is lower than this threshold.

To confirm this hypothesis we provide further data which clarify at which values of strain buckling starts to occur in our experiment. We consider the relation between the strain experienced by the nanowire and the variation of the distance between the mechanical clamps that hold the nanowire. In the pre-buckling regime, i.e. when moderate compressive stress is applied, a linear relationship describes the decrease in distance between the metal clamps and the strain experienced by the nanowire. However, when higher values of stress are applied and buckling occurs, further decrease in the distance between the metal clamps is partially accommodated by elastically deforming the nanowire away from its axis: this phenomenon is therefore related to a deviation from the linear model between the clamp displacement and the strain experienced by the nanowire.

To highlight the onset of buckling, we plot in Supplementary Fig. 1 the Raman shift of the optical polar phonons of the wurtzite (WZ) GaAs nanowire, measured by micro-Raman spectroscopy, as a function of the mechanical clamp displacement. The data-points shown in red represent the Raman shift of the A1 TO peak while the data-points shown in yellow represent the shift of the E1 LO peak. Dots and squares refer to two distinct nanowires devices measured: the reproducibility of the shift observed is a strong indication of the reliable application of elastic stress by the mechanical clamps. The observed linear relation between the clamp displacement and the Raman shifts, which is proportional to the axial strain experienced by the nanowire, is consistent with a state of compressive stress without buckling. Interestingly, only the last data point in compression does not follow the linear trend and shows the onset of a kink. This
particular data point is also shown to be poorly described by the k·p model, as shown in figure 6 of the article at around 1.2% of axial strain: we think that buckling is responsible for the lack of fit with the band structure model for this last data point.

**Supplementary Note 2: Reversibility of the photoluminescence quenching**

From the linear relation between the Raman peak energies and strain, we inferred that the WZ GaAs nanowire undergoes elastic deformations. As these deformations are by definition reversible, also the photoluminescence (PL) quenching upon compression should be reversible. We have verified this by measuring the PL during one loading–unloading cycle by increasing the nanowire compression and returning back to the unstrained condition. Spectra acquired under unstrained conditions are plotted in Supplementary Fig. 2 in green, whereas the color of the spectra acquired upon increasing compression gradually changes to blue. The left and the center panel show the PL measured with the analyzer aligned parallel and perpendicular to the nanowire axis, respectively. The right panel shows the compressive axial strain applied during the measurement sequence. As expected, the PL intensity is suppressed under compression and is recovered when returning to relaxed conditions. These observations prove that the strain effects on the band structure are fully reversible.

**Supplementary Note 3: Interface strain between core and shell in Wurtzite GaAs-Al0.3Ga0.7As Nanowires**

The nanowires of this study have a WZ GaAs core with a diameter of about 40 nm, surrounded by a uniform 40-nm-thick Al0.3Ga0.7As shell of the same crystal structure and a 3-nm-thin outer GaAs shell to prevent oxidation. There are two possible sources of strain at the interface between the two different III-V materials: the lattice mismatch between the GaAs and Al0.3Ga0.7As, and the strain generated by the difference in mechanical properties of GaAs and Al0.3Ga0.7As when uniaxial stress is applied to the nanowire. We will now show that for our material system both contributions are negligible.
In the ZB phase, all Al$_x$Ga$_{1-x}$As compounds are known to be closely lattice matched with GaAs: the largest difference in lattice constants is found between GaAs and AlAs and is smaller than 0.0078 Å, which accounts for a strain of 0.13%. To our knowledge, the lattice constants ($c$ and $a$) of WZ AlGaAs alloys have not been object of systematic measurements yet. However, many III-V alloys are characterized by a first neighbour distance between group III and group V atoms that is very similar in ZB and WZ crystals. We can therefore reasonably exclude any effect of such small interface strain between the core and shell of the nanowire we investigated.

A second possible source of interface strain can be induced by the difference in mechanical properties between GaAs and Al$_{0.3}$Ga$_{0.7}$As upon the application of uniaxial stress: a large mismatch in compliance tensor elements could lead to a state of interface strain caused by the different Poisson ratio in the two materials. For the WZ nanowires, detailed information about values of the compliance matrix elements is not yet available. However, one can relate the mechanical properties of WZ crystals to the ones of ZB using a linear relation introduced by Martin:

\[
\begin{align*}
\begin{bmatrix}
C_{11} \\
C_{33} \\
C_{12} \\
C_{13} \\
C_{44} \\
C_{66}
\end{bmatrix}^{WZ} & \approx \frac{1}{6} \begin{bmatrix}
+3 & +3 & +6 & +2 & +4 & +8 \\
+1 & +5 & -2 & +2 & +4 & -4 \\
+2 & -2 & +2 & +1 & -1 & +4
\end{bmatrix} \begin{bmatrix}
C_{11} \\
C_{12} \\
C_{44}
\end{bmatrix}^{ZB}
\end{align*}
\]

With a good approximation, this relation can be used also for the nanowire geometry. In the ZB phase, the compliance matrix elements follow a linear dependence on the aluminum concentration, increasing by 14 MPa/% for $C_{11}$, 32 MPa/% for $C_{12}$ and −5 MPa/% for $C_{44}$. For an aluminum concentration of 30%, all compliance matrix elements have values within a few tenth of percent of the one of GaAs. Using the values of ZB AlGaAs alloys and Martin’s relation we can extract the compliance tensor values relevant for our uniaxial stress experiment, shown in the Supplementary Table 2. The interfacial strain $\varepsilon_{\text{int}}$ can be approximated with the following relation:

\[
\varepsilon_{\text{int}} \approx \frac{a_{\text{Al$_{0.3}$Ga$_{0.7}$As}} (1 + \varepsilon_{xx}) - a_{\text{GaAs}} (1 + \varepsilon_{xx})}{a_{\text{GaAs}} (1 + \varepsilon_{xx})} \approx \frac{1 + a_{\text{Al$_{0.3}$Ga$_{0.7}$As}} \varepsilon_{zz}}{1 + a_{\text{GaAs}} \varepsilon_{zz}} \varepsilon_{zz} \left( \frac{c_{11}^{\text{Al$_{0.3}$Ga$_{0.7}$As}} + c_{12}^{\text{Al$_{0.3}$Ga$_{0.7}$As}}}{c_{11}^{\text{GaAs}} + c_{12}^{\text{GaAs}}} \right) - 1 < 10^{-4}\% \quad (5)
\]
Due to the small difference in the values of elastic constants, the interface strain induced by uniaxial strain deformation can be safely neglected.

In conclusion, due to the almost perfect lattice match and compliance tensor match, it is reasonable to assume the absence of any interfacial strain at the core-shell nanowire interface in any of the uniaxial stress conditions reported.
Supplementary References


