Electronic Supplementary Information: *Low Ensemble Disorder in Quantum Well Tube Nanowires*

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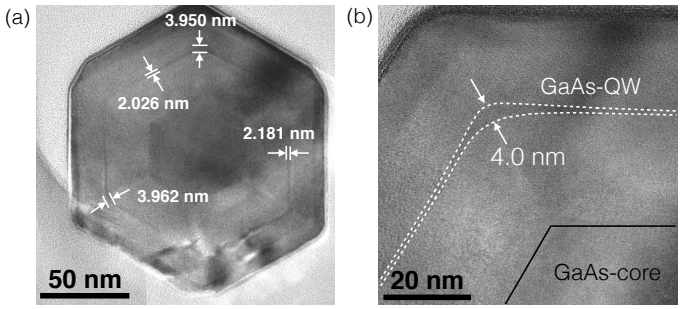

Fig. S1 TEM image of top of B50 sample

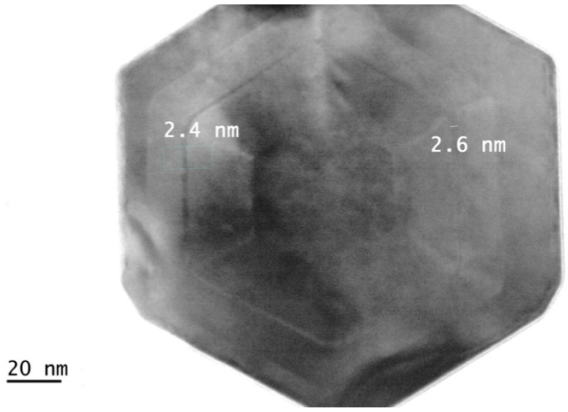

Fig. S2 TEM image of bottom of B50 sample

S1 TEM

Figure S1(a) corresponds to a low magnification bright field TEM image of a representative cross-section of the sample B50. The thickness of the GaAs QW has been measured in different regions. The variations in thickness are found to be around 4 nm and 2 nm in the edges and in the facets, respectively, confirming the disorder in the GaAs QW. In the HR-TEM image performed in one of the edges of the nanowire cross section, figure S1(b), the variation in the QW thickness (marked by white dashed lines) between the edge and the facets is clearly visible.

Figures S2 and S3 are additional TEM images of sample B50 taken from the top and bottom of a nanowire. These images demonstrate the inhomogenous well width around the nanowire.

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S2 1D Finite Square Well Model

For a semiconductor the Fermi-Dirac distribution for electrons in the conduction band and holes in the valence band is given by,

$$f_{\mathrm{e,h}} = \frac{1}{\exp((E - E_{\mathrm{f}}^{\mathrm{c,v}})\beta) + 1} \,, \tag{1}$$

where $\beta = 1/k_{\mathrm{B}}T$, T is the electron temperature and $E_{\mathrm{f}}^{\mathrm{c,v}}$ is the Fermi energies of the electrons and holes. In the high temperature limit we can ignore the $+1$ in the denominator, and the electrons and hole occupancies will follow Boltzmann statistics,

$$f_{\mathrm{e,h}} \propto \exp(-E\beta) \,. \tag{2}$$

The rate of emission is proportional to the occupancy of the electrons multiplied by the occupancy of the holes. That is,

$$f(E) \propto f_{\mathrm{e}} f_{\mathrm{h}} \propto \exp(-(E_{\mathrm{e}} + E_{\mathrm{h}})\beta) \,, \tag{3}$$

$$f(E) \propto \exp(-(E - E_{\mathrm{g}})\beta) \,, \tag{4}$$

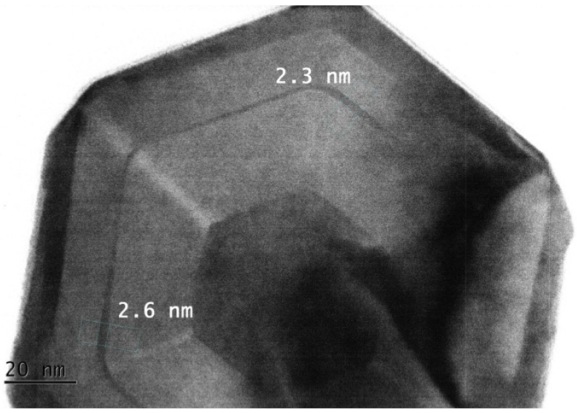

Fig. S3 TEM image of top of B50 sample

where E is the energy of the photon emitted on recombination and E_g is the band gap of the semiconductor material. For a semiconductor the energy dependence of the emission spectrum in the classical limit is proportional to the Boltzmann distribution, with an energy-offset equal to the band gap energy, multiplied by the joint density of states for the electrons and holes:

$$I(E) \propto g(E) f(E) \, , \tag{5}$$

where $f(E)$ is as above and $g(E)$ is the joint density of states for the electrons and holes. The core will have a 3–dimensional density of states but the QWT layer is confined in one direction so we need to use the 2–dimensional density of states for this case.

S2.1 Density of States

Consider an N–dimensional (N-D) box of side L (Volume$= L^{\mathrm{N}}$). A particle inside this box experiences a potential V given by,

$$V(x_i) = 0 \text{ for } 0 < x_i < L \, , \tag{6}$$

$$V(x_i) = \infty \text{ for } x_i < 0 \text{ or } L < x_i \, , \tag{7}$$

where x_i are the orthogonal coordinates of the system, for example for a 3–dimensional system $x_i = x, y$ or z. In position representation the time–independent Schrödinger equation for a non-relativistic particle for the i$^{\text{th}}$ coordinate is given by,

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(\mathbf{x})}{\partial x_i^2} + V(\mathbf{x})\Psi(\mathbf{x}) = E\Psi(\mathbf{x}) \, . \tag{8}$$

Equation (7) implies that $\Psi(\mathbf{x}) \to 0$ at $x_i = 0$ and $x_i = L$. For $0 < x_i < L$ we have that,

$$\frac{\partial^2 \Psi(\mathbf{x})}{\partial x_i^2} = -\frac{2mE}{\hbar^2}\Psi(\mathbf{x}) \, , \tag{9}$$

let us write,

$$\Psi(\mathbf{x}) = \prod_{i=1}^{N} \psi(x_i) \, , \tag{10}$$

equation (9) then reduces to,

$$\frac{\partial^2 \psi(x_i)}{\partial x_i^2} = -\frac{2mE}{\hbar^2}\psi(x_i) \, . \tag{11}$$

By considering the boundary equations (6 and 7) the normalised wave function for the i^{th} component must be given by,

$$\psi(x_i) = \frac{1}{L^{\frac{1}{2}}} \sin(k_i x_i) \, , \tag{12}$$

with $k_i = n_i \pi / L$, and so the overall wave–function is given by,

$$\psi(x) = \frac{1}{V^{\frac{1}{2}}} \prod_{i=1}^{N} \sin(k_i x_i) \, . \tag{13}$$

The volume occupied by each k-state in k-space is,

$$V_k = \left(\frac{\pi}{L}\right)^N \, . \tag{14}$$

The number of allowed states with $|\mathbf{k}| \in [k, k+dk]$ is described by the function $g(k)\mathrm{d}k$ where $g(k)$ is the density of states,

$$g(k)\mathrm{d}k = \frac{\text{V in k-space of a shell of an N-D sphere}}{\text{V in k-space occupied per allowed state}} \, , \tag{15}$$

for the case of N=3 and N=2 we have,

$$g_{3D}(k)\mathrm{d}k = \frac{4\pi k^2 \mathrm{d}k}{\left(\frac{\pi}{L}\right)^3} \, , \tag{16}$$

$$g_{2D}(k)\mathrm{d}k = \frac{2\pi k \mathrm{d}k}{\left(\frac{\pi}{L}\right)^2} \, . \tag{17}$$

Now rewriting in terms of energy using, $E = \hbar^2 k^2 / 2m^*$ and $\mathrm{d}E = \hbar^2 \mathrm{d}k / m^*$ we have,

$$g_{3D}(E)\mathrm{d}E = \frac{L^3}{\pi^2}\left(\frac{2m^*}{\hbar^2}\right) E^{\frac{1}{2}} \, \mathrm{d}E \, , \tag{18}$$

$$g_{2D}(E)\mathrm{d}E = \frac{L^2}{\pi}\left(\frac{2m^*}{\hbar^2}\right) \mathrm{d}E, \tag{19}$$

Dropping the numerical factors gives,

$$g_{3D}(E)\mathrm{d}E \propto E^{\frac{1}{2}} \, \mathrm{d}E \, , \tag{20}$$

$$g_{2D}(E)\mathrm{d}E \propto \mathrm{d}E \, . \tag{21}$$

S2.2 Model

Using the density of states $g_{3D}(E)$ for the core and $g_{2D}(E)$ for the QWT we have,

$$B_{\mathrm{Core}}(E) \propto \sqrt{E - E_{\mathrm{Core}}} \exp\left(-\frac{E - E_{\mathrm{Core}}}{k_{\mathrm{B}}T}\right) , \tag{22}$$

$$B_{\mathrm{QWT}}(E) \propto \exp\left(-\frac{E - E_{\mathrm{QWT}}^{\mathrm{e_1}\rightarrow\mathrm{hh_1}}}{k_{\mathrm{B}}T}\right) , \tag{23}$$

where T is the temperature, and E_{Core} and $E_{\mathrm{QWT}}^{\mathrm{e_1}\rightarrow\mathrm{hh_1}}$ are the band gap energies in the core and the QWT. Equation (22) can be recognised as the Maxwell-Boltzmann distribution, and equation (23) can be considered as a two-dimensional version of the Maxwell-Boltzmann distribution. The nanowires, however, do not have a perfect structure and so the spectral peaks will also be broadened by defects and disorder, which was modelled using a Gaussian, $G(E)$. To combine the two effects we take the convolution of the two,

$$I_{\mathrm{Core}}(E) \propto G_{\mathrm{Core}}(E) \otimes B_{\mathrm{Core}}(E - E_{\mathrm{Core}}) , \tag{24}$$

$$I_{\mathrm{QWT}}(E) \propto G_{\mathrm{QWT}}(E) \otimes B_{\mathrm{QWT}}(E - E_{\mathrm{QWT}}) , \tag{25}$$

where,

$$G_{\mathrm{Core}}(E) = \exp\left(-\frac{E^2}{2\sigma_{\mathrm{Core}}^2}\right) , \tag{26}$$

and,

$$G_{\mathrm{QWT}}(E) = \exp\left(-\frac{E^2}{2\sigma_{\mathrm{QWT}}^2}\right) , \tag{27}$$

The model for the measured photoluminescence is then a linear combination of these two peaks,

$$I_{PL}(E) = a_{\mathrm{Core}} I_{\mathrm{Core}}(E) + a_{\mathrm{QWT}} I_{\mathrm{QWT}}(E) , \tag{28}$$

where a_{Core} and a_{QWT} are constants dependent on the intensity of emission from the core and QWT. A least squares fit was used to determine the following parameters: $T, E_{\mathrm{Core}}, \sigma_{\mathrm{Core}}, E_{\mathrm{QWT}}, \sigma_{\mathrm{QWT}}$. Using the values for E_{Core} and E_{QWT} and a simple model for the band gap, as illustrated in Figure S5, it is possible to calculate an estimate for the well width.

Figure S4 shows a typical spectrum of a nanowire from sample B100 displayed on a logarithmic scale. The straight line seen in the high energy tails is indicative of a Boltzmann distribution ($\exp(-(E - E_0)/k_{\mathrm{B}}T)$) and is further confirmation of our models validity.

S2.3 Finite Well Model for the Band Structure

The wavefunction of excited electrons and holes in the QWT layer will undergo a perturbation due to quantum confinement effects from the finite potential well created from the difference in band gap between the $Al_{0.4}Ga_{0.6}As$ barrier layers and the GaAs QWT

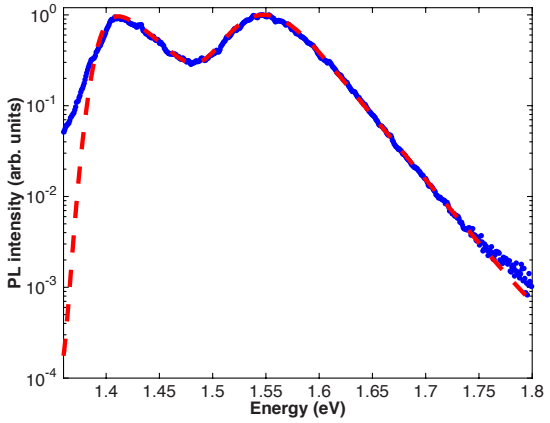

Fig. S4 PL spectrum of a nanowire from sample B100 shown on a logarithmic scale. The blue dots are the measured data and the red dashed line is the model.

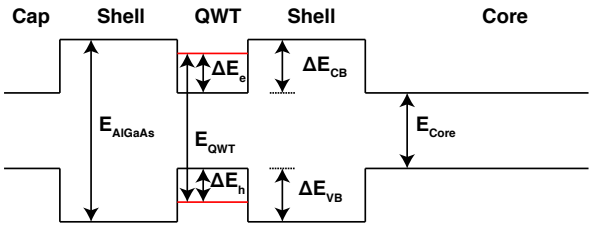

Fig. S5 A schematic diagram showing the band gap of a GaAs/$Al_{0.4}Ga_{0.6}As$ quantum well. The horizontal red lines represent the energy level of the ground state for a bound particle in the potential well where ΔE_{CB} and ΔE_{VB} are the barrier heights. CB and VB are the conduction and valence band respectively.

layers. As stated previously this confinement will increase the energy of the ground state transition. The increase in energy due to confinement is needed to be able to deduce the width of the well. Consider a finite well of width d and depth V centred on $x = 0$, and a particle whose effective mass differs in the barrier, m_{b}^* ($Al_{0.4}Ga_{0.6}As$), and the QWT, m_{q}^* (GaAs) (b = QWT; q = Core). The wavefunction of the particle is given by,

$$\psi_{\mathrm{q}}(x) = C\exp(\pm kx) \quad \text{for } |x| < d/2 , \tag{29}$$

$$\psi_{\mathrm{b}}(x) = C'\exp(\pm\kappa x) \quad \text{for } |x| > d/2 , \tag{30}$$

where,

$$k = \sqrt{\frac{2m_{\mathrm{q}}^* E}{\hbar^2}} \quad \text{and} \quad \kappa = \sqrt{\frac{2m_{\mathrm{b}}^*}{\hbar^2}(V - E)} . \tag{31}$$

Continuity conditions (ψ and its derivative with respect to x are continuous) restrict the allowed k-states to solutions of,

$$\tan\left(\frac{kd}{2}\right) = \frac{m_{\mathrm{q}}^*\kappa}{m_{\mathrm{b}}^* k} , \tag{32}$$

rearranging this equation to be in terms of energy gives,

$$\tan\left(\sqrt{\frac{2m_{\mathrm{q}}^{*}E}{\hbar^{2}}}\,\frac{d}{2}\right)=\sqrt{\frac{m_{\mathrm{q}}^{*}}{m_{\mathrm{b}}^{*}}\left(\frac{V}{E}-1\right)}\,. \tag{33}$$

The model for the quantum well we used is shown in Figure S5. The electrons are bound to a potential well of depth ΔE_{CB} and the holes are bound to a well of depth ΔE_{VB}. The values we measure from the photoluminescence are E_{QWT} and E_{Core}. From these values we can deduce the width of the well by solving the following set of simultaneous equations:

$$\Delta E = E_{\mathrm{QWT}} - E_{\mathrm{Core}} = \Delta E_{\mathrm{e}} + \Delta E_{\mathrm{h}}\,, \tag{34}$$

$$\tan\left(\sqrt{\frac{2m_{\mathrm{q,e}}^{*}E_{\mathrm{e}}}{\hbar^{2}}}\,\frac{d}{2}\right)=\sqrt{\frac{m_{\mathrm{q,e}}^{*}}{m_{\mathrm{b,e}}^{*}}\left(\frac{\Delta E_{\mathrm{CB}}}{E_{\mathrm{e}}}-1\right)}\,, \tag{35}$$

$$\tan\left(\sqrt{\frac{2m_{\mathrm{q,h}}^{*}E_{\mathrm{h}}}{\hbar^{2}}}\,\frac{d}{2}\right)=\sqrt{\frac{m_{\mathrm{q,h}}^{*}}{m_{\mathrm{b,h}}^{*}}\left(\frac{\Delta E_{\mathrm{VB}}}{E_{\mathrm{h}}}-1\right)}\,, \tag{36}$$

where the subscripts for the effective mass q and b denote the regions for the QWT layer and the boundary layer respectively, and the subscripts e and h denote the electron and hole respectively. Taking the inverse tangent of the latter two equations and substituting the first equation in, we can solve numerically for E_e and E_h. Substituting these back in and rearranging we can find the width of the well, d given by,

$$d = 2\sqrt{\frac{\hbar^{2}}{2m_{\mathrm{q,e}}^{*}E_{\mathrm{e}}}}\arctan\left(\sqrt{\frac{m_{\mathrm{q,e}}^{*}}{m_{\mathrm{b,e}}^{*}}\left(\frac{\Delta E_{\mathrm{CB}}}{E_{\mathrm{e}}}-1\right)}\right)\,. \tag{37}$$

S2.4 Surface-Area to Volume

The shape of the nanowire may be approximated by a hexagonal prism. The surface area and volume are given by,

$$S = 6l \times 2R\tan(30)\,, \tag{38}$$

$$V = 6l \times R^{2}\tan^{2}(30)\,, \tag{39}$$

So the surface area to volume ratio of the core is,

$$SV_{\mathrm{Core}} = \frac{6l \times 2R\tan(30)}{6l \times R^{2}\tan^{2}(30)} = \frac{2}{R\tan(30)}\,, \tag{40}$$

Now modelling the QWT layer as a hollow hexagonal prism of thickness d, inner radius R and outer radius R+d, the surface area to volume ratio is given by,

$$SV_{\mathrm{QWT}} = \frac{6l \times 2(R+(R+d))\tan(30)}{6l \times ((R+d)^{2}-R^{2})\tan^{2}(30)}\,, \tag{41}$$

$$SV_{\mathrm{QWT}} = \frac{2(2R+d)}{(2Rd+d^{2})\tan(30)} = \frac{2}{d\tan(30)}\,. \tag{42}$$

As such, the ratio of the surface area to volume ratio of the QWT and the core is $R/d = 20$ to 100.

S3 Band Gap and Disorder

Figure S6 shows the average values for the band gap and disorder obtained along with one standard deviation either side of the average value.

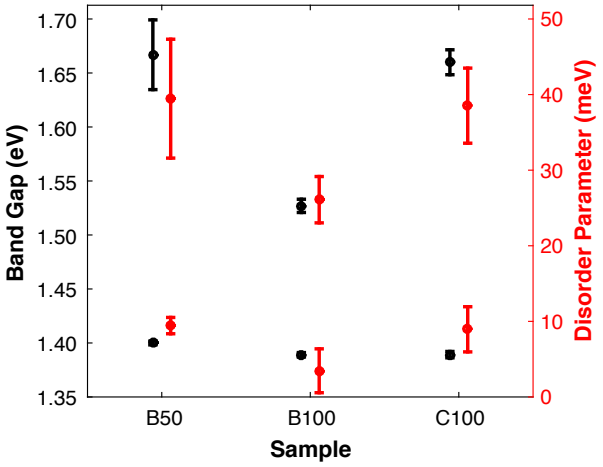

Fig. S6 The mean values and one standard deviation either side of the band gaps and disorder parameters measured for the core (lower points) and QWT (upper points).

S4 Effect of Aluminium variations (ADDED)

Here, we calculate the effect of aluminium concentration variations on the energetic disorder of each nanowire. Figure S7 shows the range of energy shifts expect for the QWT for an aluminium concentration of 0.40 ± 0.06.

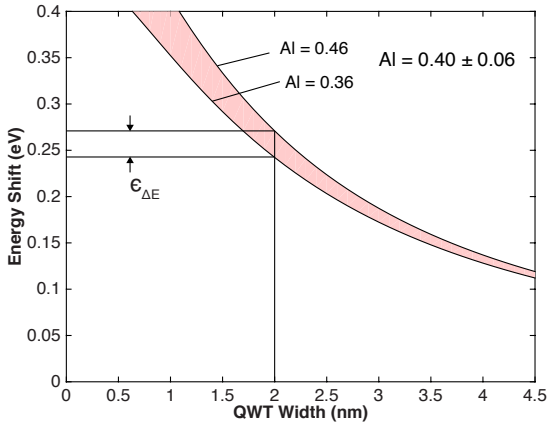

Fig. S7 Energy shift of band gap of QWT with respect to the band gap of GaAs against the QWT. $\varepsilon_{\Delta E}$ shows the energetic distribution of shifts for different aluminium concentrations

Table S1 Contribution of aluminium variations to the disorder parameter

Sample	Width (nm)	σ (meV)	$\varepsilon_{\Delta E}$ (meV)	$\varepsilon_{\Delta E}/sigma$
B50	2.1	39	26.7	0.68
B100	4.0	26	8.8	0.34
C100	2.0	39	28.7	0.74

S5 Simulations

Simulations were performed using the software package nextnano++ in 2D. The lattice temperature was set at room-temperature. Charge carriers were generated uniformly in the nanowire to simulate above band gap CW laser excitation. Measurements of the core and QWT were isolated by setting the material of the one not being measured as the same material as the barrier layer.