Non-Radiative Step facets in Semiconductor Nanowires

Supplementary Information

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1) Ortho and Para twins.

Formally, an ortho twin can be produced in a crystal with stacking sequence *...Aα Bβ Cγ Aα Bβ...* by making a cut on a {111} plane between group III and V atoms that lie on the same type of site (e.g. *C* and *γ*), followed by a rotation of one part by 180° and joining the two parts together once more. This creates a stacking sequence *...Aα Bβ Cγ Bβ Aα...* as shown in Fig. S1a. This is distinct from a twin produced by a mirror on the {111} plane, which produces a sequence *...Aα Bβ CC βB αA*…, known as a para twin (Fig. S1b). Para twins on {111} have never been observed due to the large energy of the III-III or V-V bonds that would be required for every atom on the boundary plane. See e.g. [1,2]

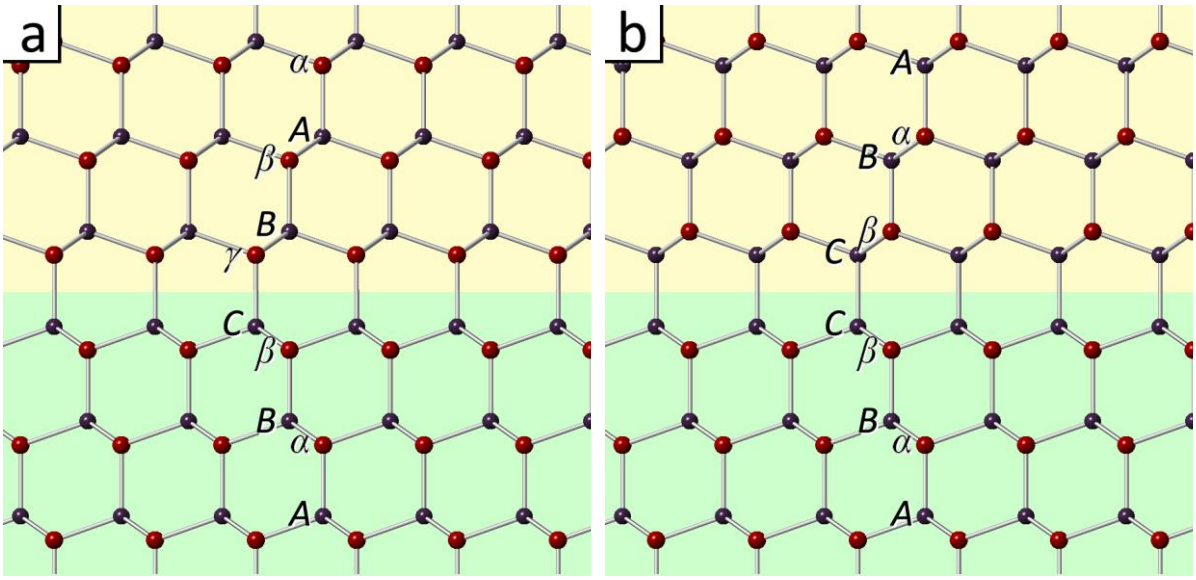

Figure S1. <110> projection of a) an ortho twin and b) a para twin in the III-V zinc blende structure.

2) Interfacial defects.

Any interfacial defect that lies between symmetrically-equivalent interfacial structures can be characterised by a combination of symmetry operations, one each from the space group of the two crystals (often denoted white, λ and black, μ) on either side of the interface.[3] As shown in Fig. S2, for each crystal it is possible to describe the relationship between the surfaces on either side of the step by a symmetry operator (since the interfaces on either side of the step are equivalent). In a planar interface these symmetry operations, represented by e.g. Seitz operators[4] W_λ and W_μ^{-1}, must leave the interfacial orientation unchanged, but they may shift its position (i.e. introduce a step). In general, the complete defect will be characterised by an operation Q;

$$Q = W_\lambda P W_\mu^{-1} P^{-1} \qquad \text{(S1)}$$

where the transformation P allows the W_μ^{-1} operation to be written in the λ reference frame (in the case of an ortho twin, P is a 180 degree rotation about the [111] axis). For the defect to be a dislocation, solutions are restricted to the case where Q is a vector, **b**. Figure S2 shows the case where the operations W_λ and W_μ^{-1} are simple translation vectors of the crystal, although more complicated scenarios are possible in non-symmorphic structures where mirror-glide and screw axes can also describe interfacial steps.[3] In the simple case where the step is characterised by lattice translations (Fig. S2), $\mathbf{t}_\lambda$ and $\mathbf{t}_\mu$ are the *step vectors* for each crystal; the Burgers vector of the interfacial dislocation is a result of the mismatch between these two vectors. For a crystalline material, surface steps are topologically conserved; a step can change its orientation on the surface but is always characterised by the same step vector. They can only form a closed loop, or end at the edge of the surface. These rules produce the similar well-known topological constraints on dislocations, as may be appreciated by considering the case where both λ and μ crystals are identical in structure and orientation.

A step will have no defect character if both step vectors are the same, i.e. $Q = 0$, or more generally

$$W_\lambda = PW_\mu^{-1}P^{-1} \quad \text{(S2)}$$

Equation S2 allows the constraints for dislocation-free steps to be derived for any interface and crystal structure. For steps in fcc twin interfaces, this occurs when the step vector is $\mathbf{t}_\lambda = \mathbf{t}_\mu = [111]$ (or indeed any multiple of [111]), i.e. three monolayers high. Eq. S2 is not satisfied for steps of other heights. For 'complete' steps, i.e. those which satisfy Eq. S2, it is possible to define an overall step vector $\mathbf{t} = \mathbf{t}_\lambda$.

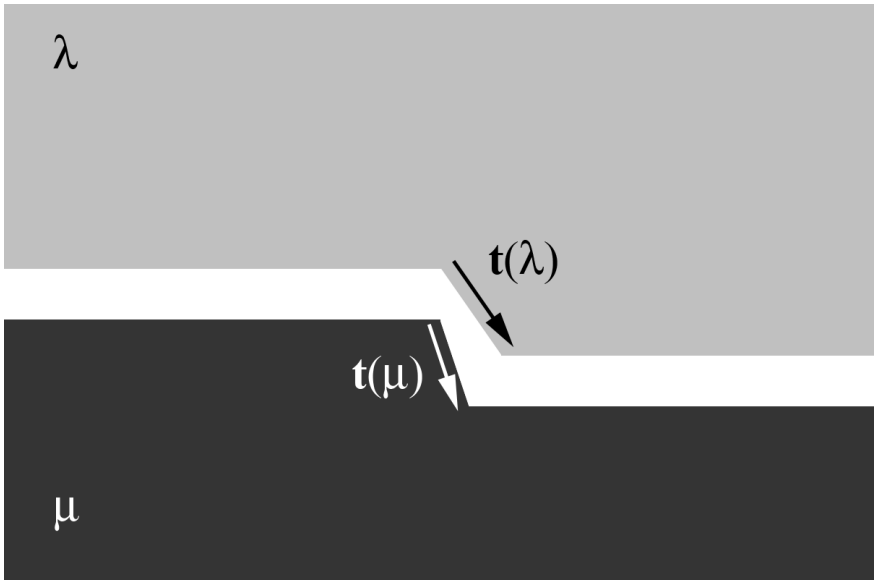

Figure S2. An interfacial step that has dislocation character, with Burgers vector **b** given by the difference between step vectors for each crystal surface $\mathbf{b} = \mathbf{t}_\lambda - P\mathbf{t}_\mu$. Line direction is out of the image.

3) $[1\bar{1}0]$ projection of a twin terminated by a $\Sigma 3$ $(11\bar{2})$ facet

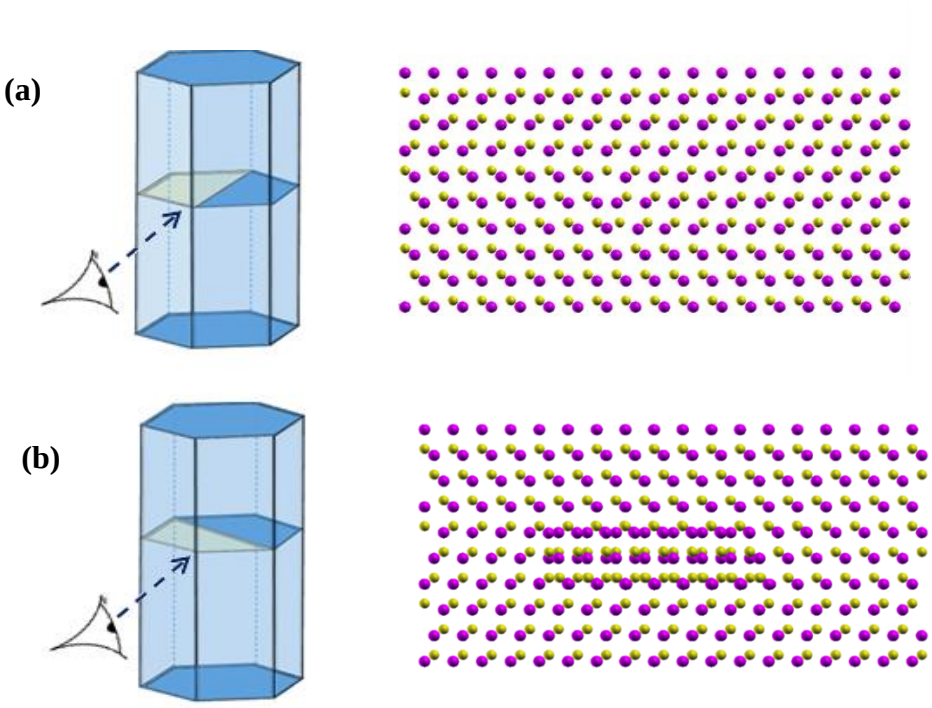

Figure S3. Two different situations have been displayed **(a)** with its end parallel and (**b)** not parallel to the electron beam.

4) Observations in other NWs

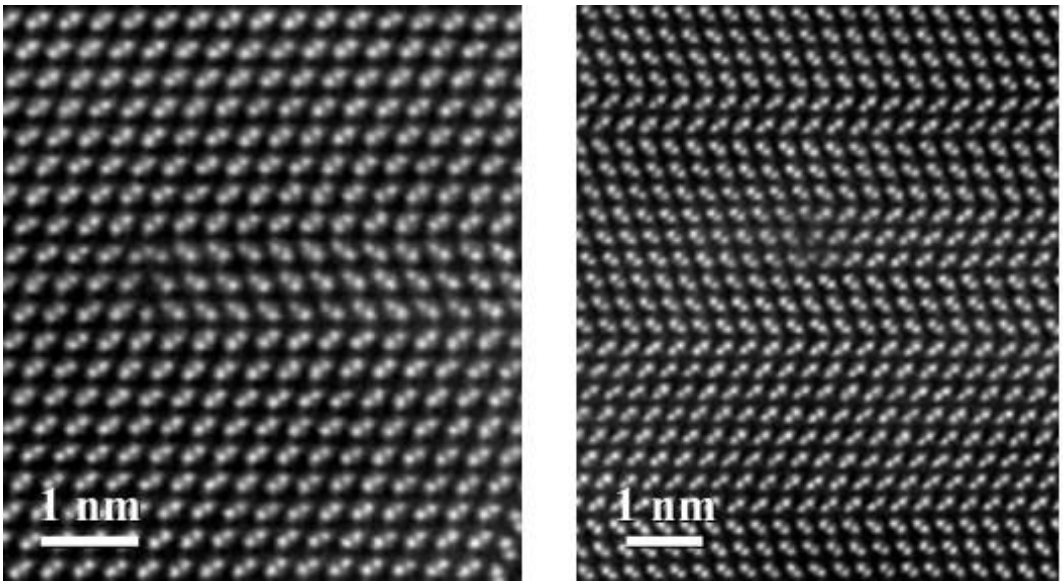

Figure S4. Two further examples of twins terminating in the interior of a GaAs NW that obey the three-monolayer rule.

Following our discovery of these defects in the GaAsP NWs mentioned in the main manuscript, we have also noticed them in other III-V zinc-blende NWs with different growth conditions and compositions. Two examples are given in Fig. S3 of twins terminating in a NW that obey the three-monolayer rule, with the same structure as shown in Fig. 4 in the main manuscript.

5) Comparison of relaxed DFT model and experimental data

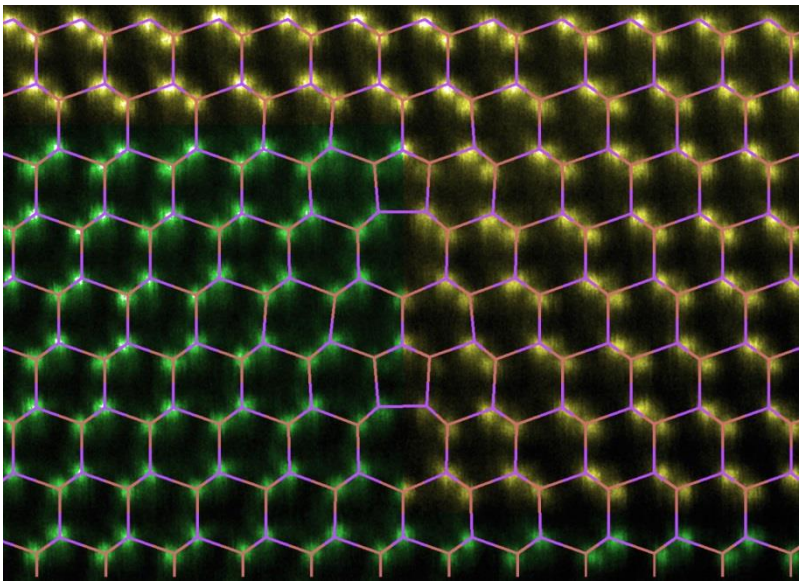

Figure S5. A colorized version of Fig. 2 with the relaxed DFT model overlaid in line form. Distortions in the STEM image, due to specimen drift during image acquisition, were removed by applying a vertical stretch of 2.7% and a horizontal skew of 2.2°.

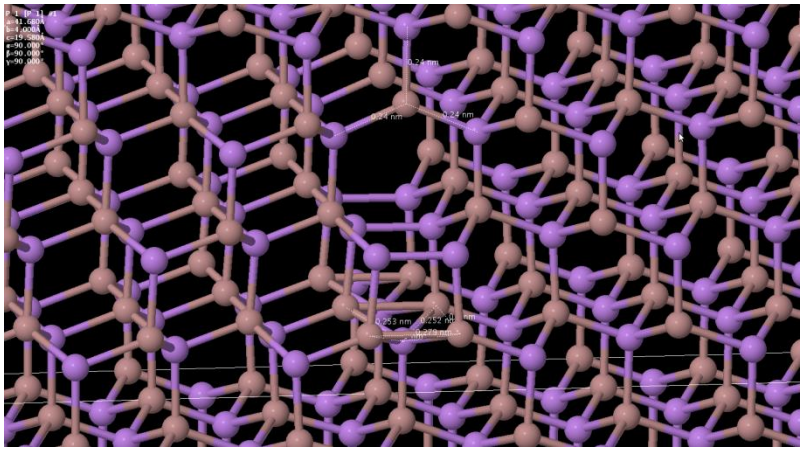

Figure S6. Perspective view of the relaxed DFT model showing atom coordination.

1. Holt, D.B. Defects in Epitaxial Films of Semiconducting Compounds with Sphalerite Structure. *Journal of Materials Science* **1**, 16 (1966).

2. Shimamura, K., Yuan, Z.S., Shimojo, F. & Nakano, A. Effects of twins on the electronic properties of GaAs. *Appl. Phys. Lett.* **103** (2013).
3. Karlsson, L.S. et al. Understanding the 3D structure of GaAs < 111 > B nanowires. *Nanotechnology* **18** (2007).
4. Litvin, D.B. & Kopsky, V. Seitz notation for symmetry operations of space groups. *Acta Crystallographica Section A* **67**, 415-418 (2011).