Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information to "Heterotwin Zn_3P_2 superlattice nanowires: the role of indium insertion in the superlattice formation mechanism and their optical properties."

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Parameter definition

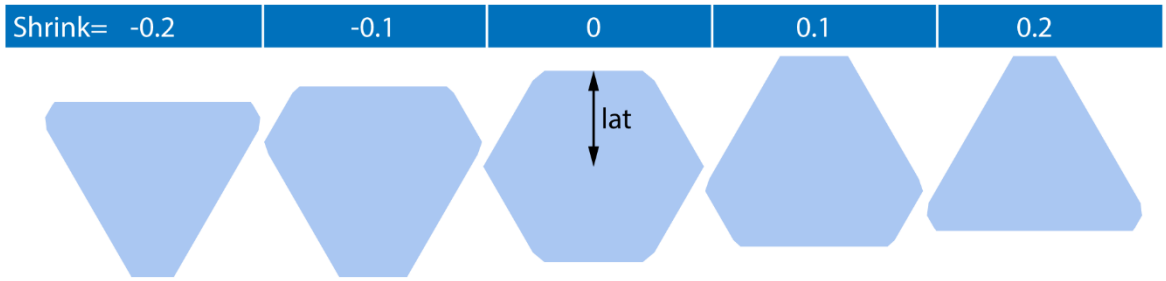

Figure S1. Illustration of the parameters used to model the droplet behaviour.

Core-loss electron energy-loss spectra

Fitting of the EEL maps are done using the peak at 443 eV for In and 1020 eV for Zn. EEL spectra after denoising are shown in Figure S2, showing the In (a) and Zn signal (b). The fitting is done using the software Gatan Digital Micrograph v2.32.

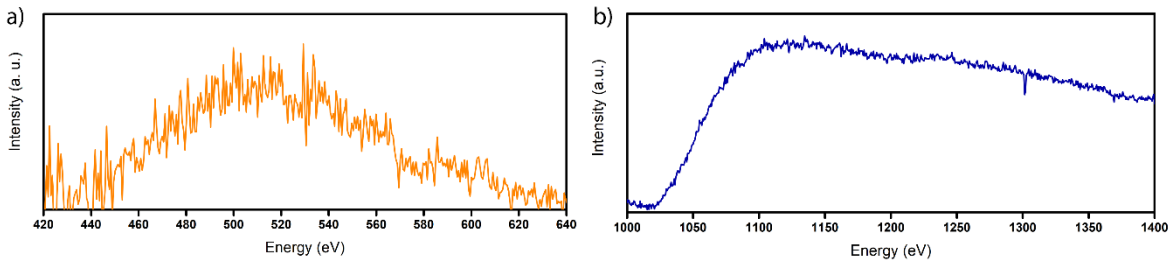

Figure S2. (a) EEL spectrum showing the In peak and (b) EEL spectrum showing the Zn peak used for mapping.

Oscillation Modelling

In Figure S3a we show a HR-TEM image of a zigzag Zn_3P_2 nanowire. We can clearly observe the presence of a sharp interface between regions having different crystal orientation (having different contrast as well). This interface occurs where the heterotwin forms and produces the change the crystal orientation. To investigate the driving forces at the origin of this growth process, we looked for a periodicity rule in the insertion of these

heterotwins as a function of the length of the nanowire. Due to the tapering effect influencing the width of the nanowire along its growth axis, we decided to measure the position and the nanowire's width at which the heterotwin is inserted through the software ImageJ. In Figure S3b we show the data points collected and the periodic function fitting the data.

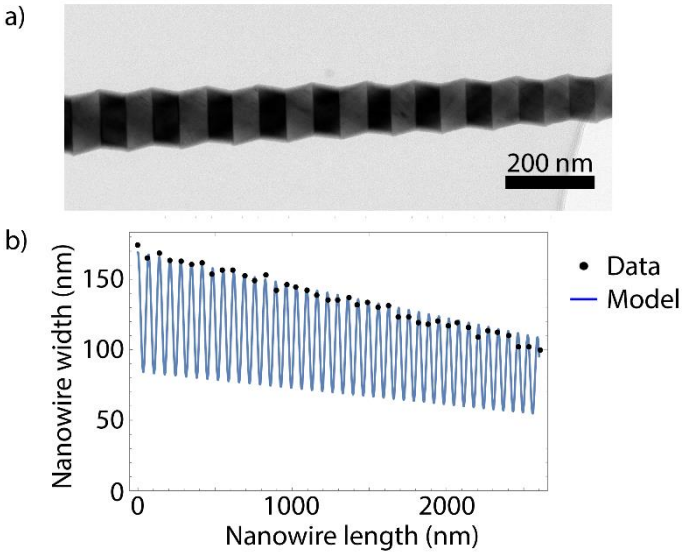

Figure S3. a) TEM image of zigzag Zn_3P_2 nanowire grown by MBE and b) plot of the development of an approximation of the nanowire's width as a function of the nanowire's growth axis: the dots represent the measurements taken on the sample shown in a) with fitting function reported in equation (1).

The selected periodic function (eq. 1) has a linear decay in the amplitude and an exponential decay in the frequency of insertion of the heterotwin. W_o and h_o are the initial width of the nanowire and the initial separation between the first two consecutive heterotwins observed in the nanowire. The fitting to the data produces $\pi/2.02$ (89°) for the tapering factor, which corresponds to the tapering angle measured in zigzag nanowires through SEM analysis (i.e., the amplitude linear decay); and 2×10^{-5} for the continuous decay rate of the separation, characterizing the exponential decay in the heterotwin insertion periodicity. We believe that the tapering factor and the continuous decay rate coefficient depends on the MBE growth conditions, i.e. temperature and II-V ratio.

$$W(x) = \left(W_0 - \frac{W_0 - \frac{W_0}{2}}{2} - \frac{x}{\tan\frac{\pi}{2.02}}\right)\left(1 + \frac{1}{3}\cos\frac{2\pi x}{h_0 e^{-2\times10^{-5}x}}\right) \quad (1)$$

Casino simulations of energy deposition in a superlattice nanowire

The simulations performed using CASINO software (V3.3) are presented in Figure S4. It can be observed that the extent of the beam interaction volume in Zn_3P_2 does not exceed 50 nm in depth and laterally at an acceleration voltage of 3kV. The assumption that no energy reaches through the sample at this acceleration voltage is thus well verified for most probed points on the CL map. Additionally, the total amount of energy deposited in the sample varies by 17% between outwards and inwards facing apices. This is explained by the variation in backscattering coefficient (η), which is largely influenced by the local geometry. We make the argument that the CL emission should follow the energy deposited by the beam. Accordingly, the superlattice nanowire local geometry is sufficient to explain the dark edge-contrast observed in the panchromatic CL map (Figure 3).

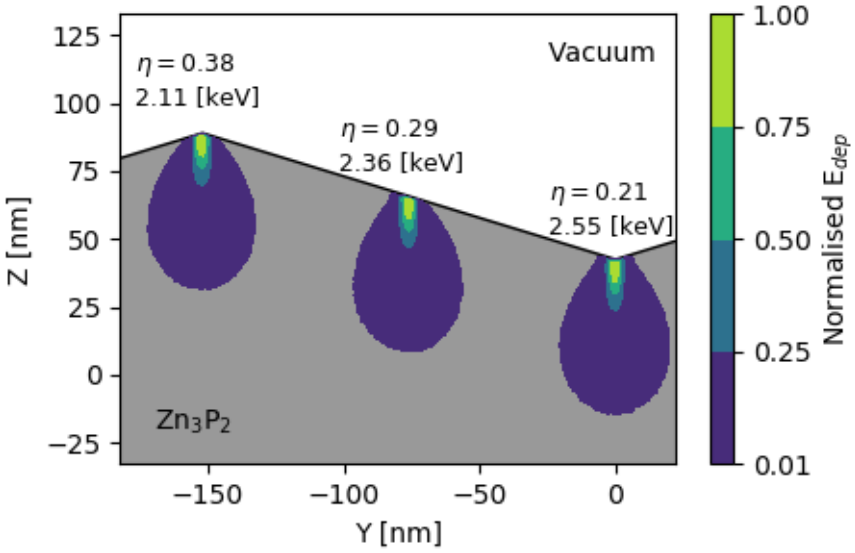

Figure S4 CASINO Simulation of energy deposited in the sample for different edge configuration. Coloured surfaces show the decrease in energy density deposited in the sample, normalised to the maximum. Annotations show the fraction of backscattered electrons (η) and the total amount of energy (in keV) deposited in the sample per electron, for each edge configuration. It is observed that outwards facing apices (left) show enhanced backscattering compared to inwards facing apices (right) or facets (middle). Simulations where performed using a collimated electron beam of 10 nm diameter at 3 kV and a density of 4.55 g cm^{-3} for Zn_3P_2. Due to the limited possibilities of simulating complex geometries in CASINO 3, we model the sample with truncated pyramids. This approximation reproduces well local edge configuration, but would not be valid in experiment conditions where a significant part of the beam energy is transmitted through the sample, e.g. at high beam energies.