Electronic Supplementary Information for:

Tuning the Electronic Properties of ZnO Nanofilms via Strain-induced Structural Phase Transformations and Quantum Confinement

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S1. Convergence tests.

DFT calculations were performed using a 500 eV plane wave energy cut-off and a force convergence criterion of 0.01 eV $Å^{-1}$. Increasing the cut-off to 600 eV for nanofilms of both BCT-ZnO and hex-ZnO polymorphs result in a variation of total energy of less than 3×10^{-3} eV/ZnO. Increasing the force convergence criterion for optimisations to 1E-5 eV $Å^{-1}$ led to variations in total energy of less than 5×10^{-7} eV/ZnO.

The variation in total energy with respect to the **k**-point grid settings employed in the current study are summarised in tables S1 and S2 below.

	k-point grid setting					
	2×2×1	3×3×1	4×4×1	5×5×1	7×7×1	9×9×1
ΔE_{ZnO}(eV/ZnO) - optimisations	>0.01	Current work	$>5\times10^{-5}$			
ΔE_{ZnO}(eV/ZnO) - single point calculations on optimised structures				$>5\times10^{-5}>$	$>5\times10^{-5}$	Currrent work

Table S1. Difference in total energy for the 5L BCT-ZnO nanofilm with 0% strain with respect to k-point mesh settings. The energy obtained using settings employed in the current work are taken as a reference.

	k-point grid setting					
	2×2×1	3×3×1	4×4×1	5×5×1	7×7×1	9×9×1
ΔE_{ZnO}(eV/ZnO) - optimisations	>0.01	Current work	$>5\times10^{-5}$			
ΔE_{ZnO}(eV/ZnO) - single point calculations on optimised structures				$>5\times10^{-5}>$	$>5\times10^{-5}$	Current work

Table S2. Difference in total energy for the 5L hex-ZnO nanofilm with +7% strain with respect to k-point mesh settings. The energy obtained using settings employed in the current study are taken as a reference.

S2. Comparison between PBE and PBE0

We compare the variation in total energy of a 5L nanofilm using both PBE-based DFT calculations (as employed in the current work) and calculations using the hybrid PBE0[1] functional for a range of in-plane strains. The PBE0-based calculations used the FHI-AIMS[2] all-electron DFT code with a Tier1/light atom-centred numerical basis set. Between strains of -8 and +4% we see a small difference of ≤0.02 eV/ZnO between the two sets of calculations. For the highest compressive strain this difference slightly increases to 0.04 eV/ZnO. Overall, the predicted energetic trends are very similar when employing both functionals.

Strain (%)	-8	-2	+3	+4	+9
$\Delta E_{\mathbf{BCT-ZnO}}$(eV/ZnO) PBE0	0.16	0.00	0.05	0.05	0.11
$\Delta E_{\mathbf{BCT-ZnO}}$(eV/ZnO) PBE	0.18	0.01	0.03	0.04	0.15
ΔE(PBE-PBE0)	0.02	0.01	-0.02	-0.01	0.04

Table S3. Variance in total energy of 5L nanofilms for a range of in-plane strains with respect to that of bulk BCT-ZnO ($\Delta E_{\mathbf{BCT-ZnO}}$) calculated using: i) the PBE-based computational set-up described in in the current work, and ii) using calculations employing the hybrid PBE0 functional.

S3. Out-of-plane Zn-Zn interactions

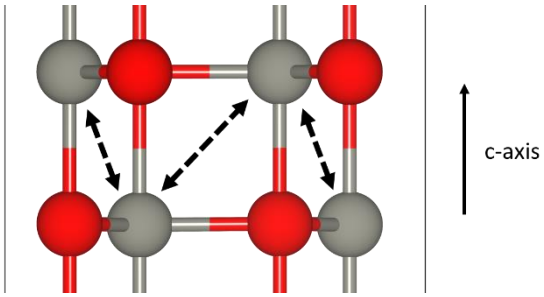

Figure S1. Out-of-plane Zn-Zn interactions (dashed arrows) giving rise to Zn4s-Zn4s bonding orbital overlap in the layered-ZnO and hex-ZnO nanofilms.

References

1. C. Adamo, V. Barone,Toward Reliable Density Functional Methods without Adjustable Parameters: The PBE0 Model. *The Journal of Chemical Physics* 1999, **110**, 6158–6170.

2. V. Blum, R. Gehre, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler, Ab initio molecular simulations with numeric atom-centered orbitals, *Comput. Phys. Commun.*, 2009, **180**, 2175–2196.