

Polarization-Induced Charge Distribution at Homogeneous Zincblende/Wurtzite Heterostructural Junctions in ZnSe Nanobelts

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Tailoring of charge distribution has been a hot topic for semiconductor-based materials ever since the discovery of Si p-n junctions in the 1940s.^[1] The p-n junction can be created in semiconductor single crystals by doping, thereby introducing impurity levels into the band gap, and forming a depletion region with built-in potential difference across the junction. Heterojunctions consisting of materials with different band gaps exhibit considerable valence and/or conduction band offsets at the interfaces, which cause electrons or holes to reside in the same material^[2] (type I band alignment) or become separated in different materials^[3,4] (type II band alignment). The strain due to lattice mismatch at the interface can also introduce band-bending, facilitating higher density of charge localization at the interfaces.^[5] Here we demonstrate that the growth of homogeneous wurtzite (WZ)/zincblende (ZB) heterostructural junctions in compound semiconductors represents a viable alternative approach to achieving tailored charge distribution at the nanoscale.

Without the common problems associated with compositional changes and strain control, the controlled growth of twinned structures and polytype superlattices in Group III–V (InP, InAs, GaAs) nanowires (NWs) leads to homogeneous heterostructural junctions.^[6–9] Redshift of the photoluminescence emission energy is observed when the percentage of WZ material as compared to ZB material is increased.^[9] A blue-shift of the photoluminescence of the rotationally twinned

heterostructure is reported to be dependent on the excitation power.^[10] These novel optical properties are attributed to the comparatively large band offsets between the ZB and WZ polytypes, which lead to charge redistribution along the NWs. This study reports electron holography observation of a saw-tooth-like potential profile across homogeneous ZB/WZ heterostructural junctions in ZnSe nanobelts, induced by the spontaneous polarization (SP) present in the WZ regions. The choice of ZnSe is critical for this investigation since ZB/WZ interfaces in ZnSe nanobelts have been calculated to have close to zero valence and conduction band offsets.^[11] Thus, contributions from band offsets are likely to be minimal, making it possible to measure the SP-related electrostatic field separate from any other charge redistribution mechanisms.

The WZ structure is expected to possess intrinsic SP since the four tetrahedral bonds do not have equivalent bond-to-bond charge transfer, and ionic relaxation can introduce SP along the (c-axis) stacking direction.^[12] Conversely, the tetrahedral bonds are symmetric for the ZB structure. Thus, the cubic ZB structure has no bulk SP when grown along $\langle 111 \rangle$. However, it still provides perfect interface matching with $\langle 0001 \rangle_{\text{WZ}}$, i.e., surface and truncation effects can be avoided,^[12] making it a perfect medium for determination of SP in the WZ region.

An atomic model for the WZ/ZB/WZ interfaces is presented in Figure 1a. The blue and yellow balls represent Zn^{2+} and Se^{2-} , respectively. As a result of the asymmetric tetrahedral bonding in the WZ unit cell, dipoles should accumulate along the $[000-1]$ direction, leaving positive charges at the WZ/ZB junction, and negative charges at the ZB/WZ junction. Thus, there should be linearly increasing electrostatic potential and negative electrostatic field in the WZ region, and linearly decreasing electrostatic potential and positive electrostatic field in the ZB region, induced by those polarization charges, as shown in Figure 1b. Theoretical calculations of potential profiles across the ZB/WZ interface and charge densities at the junctions have been previously reported for BeO ,^[13] SiC ,^[12,14,15] BN and GaN ,^[14] all of which show the same saw-tooth-like features as sketched in Figure 1b.

An investigation of atomic arrangements and polarity continuity at the ZB/WZ interface of a specific ZnSe nanobelt was performed using aberration-corrected high-angle annular-dark-field (HAADF) imaging, as shown in Figure 1c (right). The left region is projected along $[-110]_{\text{ZB}}$, while the right region is projected along $[-2110]_{\text{WZ}}$. The intensity line profiles along an array of Zn–Se atomic columns in the ZB region (labeled as 1), and dumbbells in two directions in the WZ region (labeled as 2 and 3) are shown on the left. Although the atomic numbers of Zn

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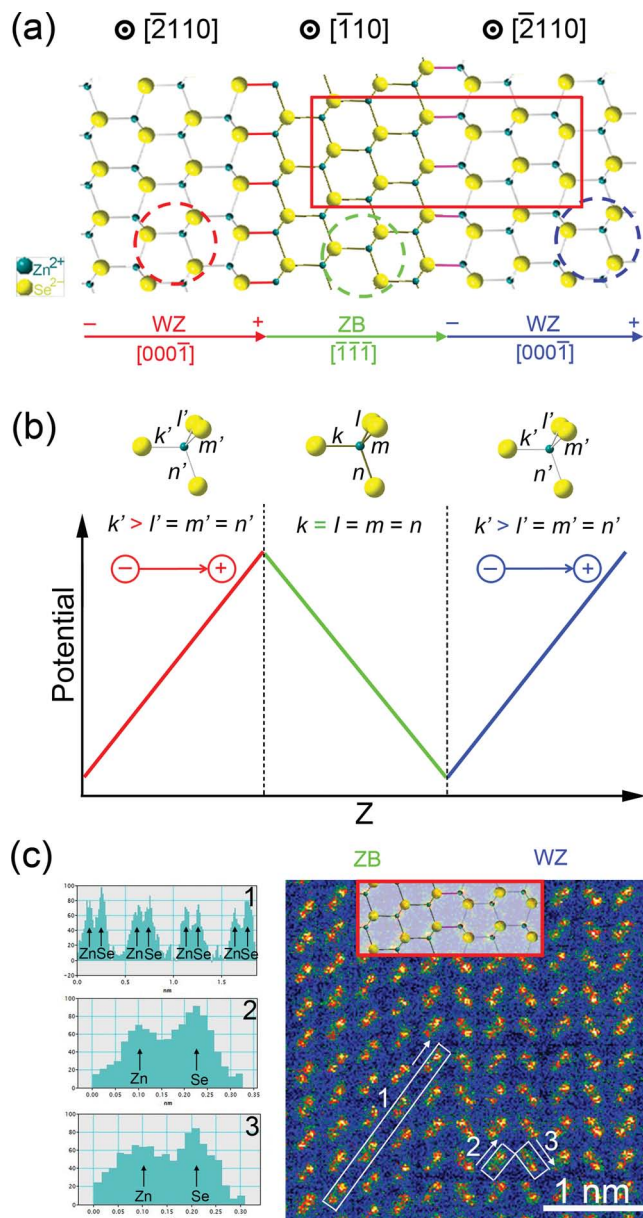


Figure 1. a) Atomic model for the WZ/ZB/WZ heterostructures projected along $[-110]_{\text{ZB}}$ and $[-2110]_{\text{WZ}}$. Directions along the interface normal are also labeled. b) Sketch of the saw-tooth-like potential profile. The green line corresponds to the central ZB region, while the red and blue lines relate to the adjacent WZ regions. One tetrahedron is shown for each region, which is extracted from the region in the dashed circle with corresponding color in (a). c) (Right) Aberration-corrected HAADF image of ZB/WZ interface showing that individual Zn-Se atomic columns are clearly resolved. The ZB/WZ heterostructure atomic model is overlapped in a red box, which is the same region as the red-boxed area in (a). (Left) The intensity line profiles along an array of Zn-Se columns in ZB region (labeled as 1), and dumbbells in two directions in WZ region (labeled as 2 and 3) are shown. Peaks on the right are always greater than the adjacent peaks on the left.

and Se are quite close (Zn: 30, Se: 34), the intensity peak on the right is apparently higher than the adjacent peak on the left, indicating that the heavier atom is located on the right. It is

significant that the crystal polarity maintains the same direction across the ZB/WZ interface, illustrated by the conformity from regions 1 to 2 and 3. Consequently, no charge accumulation due to polarity reversal would be anticipated at the interface.

Figure 2a shows an off-axis electron hologram of a ZnSe nanobelt including WZ/ZB/WZ junctions. The nanobelt was first tilted to the closest $[-110]_{\text{ZB}}/[-2110]_{\text{WZ}}$ zone axis, and then rotated slightly about the axis normal to the junctions $[111]_{\text{ZB}}/[0001]_{\text{WZ}}$ in order to avoid diffraction contrast while the junctions were kept edge-on. Figure 2b presents an high-resolution electron microscopy (HREM) image of the same nanobelt, with the bottom left corner corresponding to the amorphous layer along the edge of nanobelt. There is a WZ region of width ~ 7 nm to the right of the amorphous layer, followed by a ZB region of width ~ 22 nm, and a wider region of WZ that is only partly visible in the HREM image (see Supporting Information Figure S1 for an overview of the ZnSe nanobelt). Figures 2(c) and 2(d) are the corresponding reconstructed phase and thickness images, respectively. The thickness image was calculated based on the reconstructed amplitude image assuming a value of 67 nm (GaAs)^[16] for the inelastic mean free path (MFP) for ZnSe.^[17] The MFP value for ZnSe was not known. However, it was reasonable to employ the MFP of GaAs since ZnSe and GaAs have equal average atomic numbers, which is the primary factor in determining the magnitude of the inelastic MFP.

Line profiles for the phase shift and thickness perpendicular to the WZ/ZB/WZ junctions are shown in Figures 2(e) and 2(f), respectively. The box region used for line profiling is outlined in Figures 2(c) and 2(d), starting from the interface of the amorphous layer and the bottom WZ region. The red squares, green triangles and blue circles in Figures 2(e) and 2(f) represent the experimental data for the bottom WZ region, the sandwiched ZB region, and the top WZ region, respectively. The phase shifts in Figure 2e increase almost linearly in the WZ region, and decrease linearly in the ZB region, while the turning points coincide with the junction positions. Linear fits to the experimental data are superimposed as red, green, and blue lines. The thickness profile, on the other hand, is flat across the entire region, which implies that the thickness is effectively constant. Thereby, the decreasing (ZB region) and increasing (WZ region) phase shifts indicate that opposing electrostatic fields are present in the ZB and WZ regions, so that charges of opposite signs must be located at these junctions. The quantitative analysis would be considered later on.

For nitride-based heterostructures, the electrostatic potential across junctions is usually induced by the combination of both SP and piezoelectric polarization (PE).^[18,19] Thus, it is necessary to take possible contributions from PE into consideration in our experiment. In the linear regime, PE is related to strain by the piezoelectric tensor according to the expression:^[20]

$$P_i = \sum_j e_{ij} \varepsilon_j \quad (1)$$

where P_i stands for piezoelectric polarization, e_{ij} is piezoelectric tensor, and ε_j represents strain.

Figure 3a is an HREM image showing the ZB/WZ interface of another ZnSe nanobelt. The geometric phase analysis (GPA) procedure for mapping displacement fields and strain fields

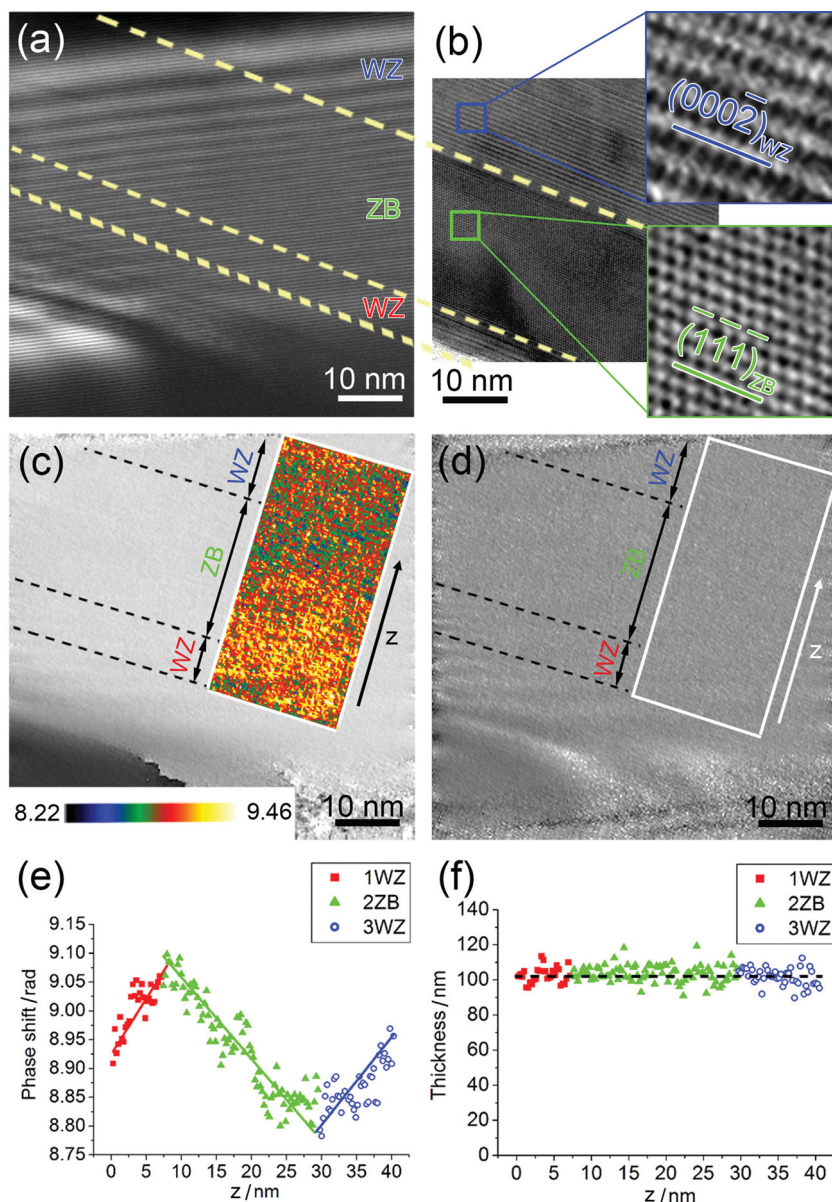


Figure 2. a) Electron hologram from region including WZ/ZB/WZ junctions. b) HREM image of the same nanobelt. The positions of the interfaces are labeled with dashed yellow lines. Regions in small green box for ZB structure and blue box for WZ structure are enlarged to clearly show the lattices. The projection is along $[-110]_{\text{ZB}}/[2110]_{\text{WZ}}$ zone axis, and the parallel $(-1-1-1)_{\text{ZB}}$ and $(000-2)_{\text{WZ}}$ planes are labeled in the related magnified images. c) Corresponding reconstructed phase image: the boxed region used for profiling is shown in color with the WZ and ZB regions labeled, and the color bar calibrated in radians is shown. d) Thickness image of the same region with the WZ and ZB regions labeled. e) Phase shift profile of the box region labeled in (c). f) Thickness profile of the box region labeled in (d), which is the same region used for the phase shift line profile.

from HREM images was utilized.^[21] Meanwhile, a GPA program compatible with Digital Micrograph was applied for calculation of the strain map. Figure 3b shows the strain map for ε_{zz} (ε_3 in equation 1), which is the normal (perpendicular to the interface) strain component along the z direction, i.e., $[111]_{\text{ZB}}/[0001]_{\text{WZ}}$, whereas the reference lattice was taken from the ZB region. The corresponding line profile across the ZB/WZ

interface is presented in Figure 3c, which is averaged over the boxed region in Figure 3b.

The value of ε_{zz} away from the interface is approximately zero, as indicated by the red dashed lines in Figure 3c, whereas the strain component ε_{zz} across a heterostructured interface should normally give a step-like profile.^[21,22] Thus, the close to zero values in the ZB and WZ regions away from the immediate vicinity of the interface indicate extremely low levels of strain in both regions, and hence negligible PE contributions to the electrostatic fields. The sharp abrupt peaks visible at the interface may result from phase shifts that originate from the deviation from periodic translational symmetry of the crystal lattices across the interface or possible slight local tilt.

Since ε_{zz} is approximately zero away from the interface, the long-range linear slopes visible in Figure 2e must be mainly induced by SP present in the WZ regions. The phase shift profile in Figure 2e can be converted to electrostatic potential using: $\varphi = C_E (V_{\text{MIP}} + V_{\text{SP}}) t$, where $C_E = 0.00728 \text{ rad (V nm)}^{-1}$ for an accelerating voltage of 200 kV, φ is the phase shift, t is the projected thickness, V_{MIP} is the mean inner potential (MIP) of the material, and V_{SP} is the electrostatic potential due to SP. Only the latter term would contribute to the electrostatic field as a slope of the electrostatic potential profile since the MIP is constant for a specific structure. Thus, the electrostatic field E can be calculated for both ZB and WZ regions based on a linear fit of the experimental phase shift data: $E_{\text{ZB}} = 0.0189 \text{ V nm}^{-1}$, $E_{\text{WZ}} = -0.0204 \text{ V nm}^{-1}$.

A possible MIP difference between the ZB and WZ structures requires to be considered as well. For calculation of MIP, the non-binding model treats a solid as consisting of neutral free atoms (upper limit), while the Radi model treats the crystal as consisting of ions with the remaining valence electrons distributed uniformly (lower limit).^[23] The MIP calculation for ZnSe reveals that the ranges of MIPs for the ZB and WZ structures are so close that the difference can be neglected in calculations. Meanwhile, any MIP difference between the ZB and WZ structures would just result in small steps at the interfaces without causing slopes in different regions. As a result, any contribution of the MIP dif-

ference to the observed electrostatic field can be excluded.

The SP in the WZ region can be calculated using:^[12,24]

$$p_{\text{sp}} = -\varepsilon_0 \varepsilon_r \Delta E = -\varepsilon_0 \varepsilon_r \left(\frac{\partial V_{\text{WZ}}}{\partial z} - \frac{\partial V_{\text{ZB}}}{\partial z} \right) \quad (2)$$

where $-\frac{\partial V_{\text{WZ}}}{\partial z}$ and $-\frac{\partial V_{\text{ZB}}}{\partial z}$ correspond to the electric fields in the WZ and ZB regions, which are $E_{\text{WZ}} = -0.0204 \text{ V nm}^{-1}$, and

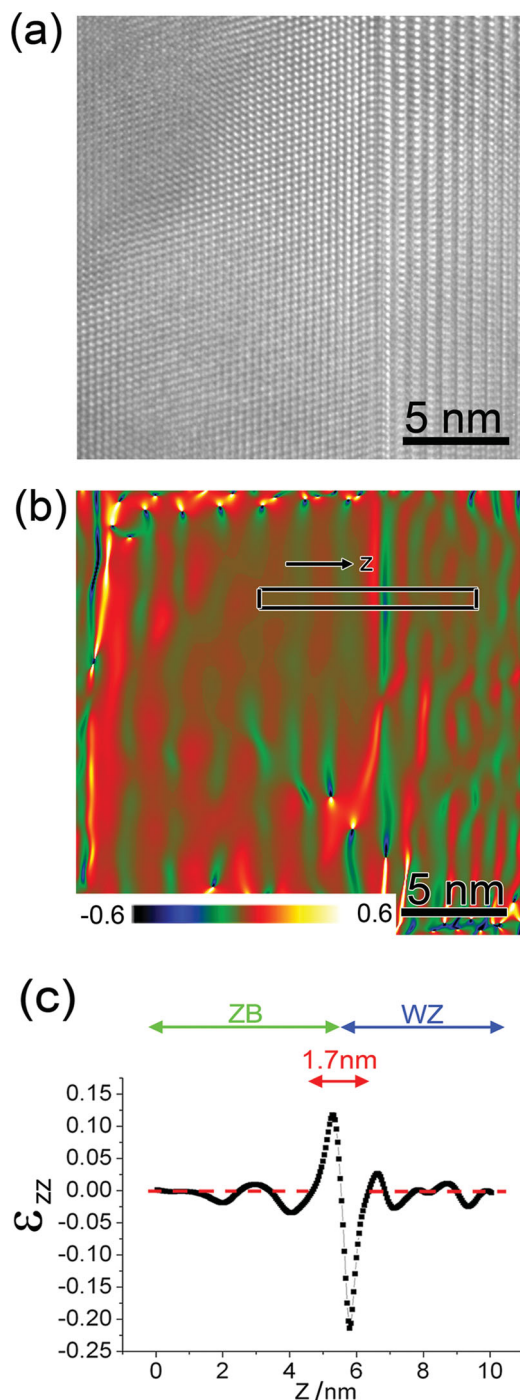


Figure 3. a) HREM image of ZB/WZ interface. b) Strain map for ϵ_{zz} of the same region of HREM imaging. c) Line profile of ϵ_{zz} of the box region labeled in (b). ϵ_{zz} away from the interface is approximately zero in both regions.

$E_{ZB} = 0.0189 \text{ V nm}^{-1}$ for our specific case, and $\epsilon_r = 9.25$ (at $T = 296 \text{ K}$) is used.^[25] Thus, the SP present in the WZ region is estimated to be $p_{sp} = -0.0032 \pm 0.00014 \text{ C m}^{-2}$, where the error $\Delta p_{sp} = \pm 0.00014 \text{ C m}^{-2}$ is calculated through error propagation from the errors in potential measurement $\Delta V = \pm 0.035 \text{ V}$ and $\Delta z = \pm 0.2565 \text{ nm}$ (the pixel size).

Since no calculated or experimental SP values are available for ZnSe, we have calculated the bulk SP value for WZ-ZnSe

and ZB-ZnSe using the Berry phase expression^[26,27] based on first-principles calculations implemented in VASP,^[28,29] as well as the SP value for WZ-ZnSe applying the supercell approach reported in Ref. 12. The bulk SP values calculated using the so-called Berry phase approach are -0.0063 and 0.0 C m^{-2} , for WZ-ZnSe and ZB-ZnSe, respectively. The calculated SP value for WZ-ZnSe employing the ZB-ZnSe/WZ-ZnSe supercell is $p_{sp} = -0.0022 \text{ C m}^{-2}$, and the simulated potential profile across the interface based on the supercell approach (see Supporting Information Figure 2S.) shows the same saw-tooth-like features as our experimental results. Since the SP value calculated by Berry phase approach provides an intrinsic value for ideal bulk WZ-ZnSe crystal, and taking into account the possible lowering effect from finite nanoscale system and possible defects in the nanobelts, the calculated value would provide an upper limit; while the SP value obtained from the supercell approach, where the supercell is constructed with two ZB unit cells and two WZ unit cells through modelling of the experimental ZB/WZ heterostructural junction, could be considered as a lower limit. Our experimental SP value falls reasonably within the range of theoretical calculations ($0.0022 < 0.0032 < 0.0063 \text{ C m}^{-2}$).

In summary, homogeneous ZB/WZ heterostructural junctions have been successfully synthesized in ZnSe nanobelts, and polarity continuity is determined through aberration-corrected HAADF imaging. The hypothesized saw-tooth-like potential profile is directly revealed at the nanoscale using off-axis electron holography. With the exclusion of possible contributions from piezoelectric polarization, and assuming that band offsets are minimal for these interfaces, spontaneous polarization is identified as the predominant factor causing the experimental profile. Furthermore, the measured spontaneous polarization for wurtzite ZnSe falls within the range of theoretical simulations. Our results suggest that the polarization-induced charge distribution at ZB/WZ heterostructural junctions could represent a viable alternative path for tailoring charge distribution in semiconductor nanostructures.

Experimental Section

The homogeneous ZB/WZ ZnSe heterostructural junctions were fabricated via thermal evaporation of ZnSe powder. Detailed growth information has been published elsewhere.^[30,31] The products were scratched off the Si substrate, sonicated in ethanol, and then deposited on copper grids with holey carbon film for electron microscopy observation. The off-axis electron holography observations and HREM imaging were carried out using a Philips CM200-FEG transmission electron microscope (TEM) equipped with an electrostatic biprism and a $2.8k \times 2.6k$ Gatan Orius SC200W charge-coupled-device camera. The sample was imaged in the diffraction mode but with the diffraction lens turned off in order to obtain a larger field of view. The interference fringe spacing was $\sim 0.57 \text{ nm}$, and the overall image magnification was set at $\sim 120 \text{ kX}$. The HREM images used for strain-map calculations were obtained using a JEOL JEM-2010 FEF (UHR) TEM. The aberration-corrected imaging was performed in the HAADF mode using a JEOL ARM200F TEM. All microscopes were operated at an acceleration voltage of 200 kV .

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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