

Superposition twinning supported by texture in ZnO nanospikes

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The morphology and real structure of wurtzite-type ZnO nanospikes grown by the recently introduced flame transport synthesis have been examined by means of advanced transmission electron microscopy (TEM). The rapid synthesis produces nanospikes showing a well defined texture which restricts TEM experiments to a preferred viewing direction of $[2\bar{1}\bar{1}3]$. Forced by the specific morphology, all of the observed nanospikes show a complicated superposition of twinned domains as an intrinsic real structural feature. The high-resolution contrasts are characterized by lamellar fringes parallel to the $(1\bar{1}01)$ planes, and the quasi-kinematic diffraction patterns contain satellite peaks based on multiple scattering. All these phenomena can be interpreted by comparison of experimental and simulated data relying on a supercell approach.

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1. Introduction

Zinc oxide (ZnO) semiconductors have been the subject of intensive research owing to their wide spectrum of manifold physical and chemical properties. In particular, comparison of the respective piezoelectric tensors and tensor components of different wurtzite-type (labelled 'w' in the following) structures has revealed useful piezoelectric properties of ZnO (Özgür *et al.*, 2005; Dal Corso *et al.*, 1994; Wang, 2004a, 2009; Ashrafi & Jagadish, 2007). While these classical piezo materials, when applied directly, are outperformed by modern ferroelectric materials, their application in magnetoelectric composite sensors is very promising. Furthermore, a direct bandgap of *ca* 3.37 eV and a large exciton binding energy of 60 mV at room temperature have promoted ZnO as a valuable candidate for already realized and envisaged devices and sensor applications (Phelps, 1982). In the fields of short-wavelength nanolasers (Özgür *et al.*, 2005), field-effect transistor devices (Jebriil *et al.*, 2010) and nanocantilevers (Hughes & Wang, 2003), these characteristic advantages are especially accentuated. In many cases, anisotropic one-dimensional nanostructures (Phelps, 1982; Xia *et al.*, 2003) of ZnO form the basis of the various applications. In order to obtain such one-dimensional nanostructures, efficient, cheap and fast production techniques are required (Özgür *et al.*, 2005; Hughes & Wang, 2003, 2010). In this respect, the vapour–liquid–solid (VLS) process has proved its functionality among other techniques (Wang, 2004b, 2010; Borchers *et al.*, 2006). The advantage of VLS is the possibility of precise and well defined

crystal-growth conditions, which are essential for deliberate control of the crystalline quality and morphology of ZnO one-dimensional nanostructures.

In the case of traditionally grown ZnO nanowires and nanobelts, four typical growth morphologies result in characteristic corresponding facets (Wang, 2004a). The most frequently observed and important growth direction of $[0001]^w$ for piezoelectric applications leads to polar $(0001)^w$ basal facets. Single-crystalline hexagonal columns in this orientation offer the highest piezoelectric voltages under deformation. However, besides morphology, specific defects determine the properties. For instance, twin boundaries are important to identify as they short-circuit the piezoelectric effect, as is well known from sputter-deposited ZnO (Molarius *et al.*, 2004). Moreover, these defects might enhance the functional properties in other fields. While an ideal growth of defect-free one-dimensional nanostructures is required for good piezoelectricity, the presence of intrinsic defects such as self-vacancies/interstitials, twin boundaries *etc.* further strengthens the capabilities for other applications, such as gas sensors, where the absence of piezoelectric voltages is necessary (Pearton *et al.*, 2005; Liu *et al.*, 2009; Comini *et al.*, 2002). Accordingly, with such a close correlation between properties, morphology and real structure, deliberate control of the growth conditions and optimization of defect concentration in a device can only be established through structural investigations. This in turn demands systematic nanoscale analysis by electron microscopy for identification and full understanding

of the defects. Several in-depth studies of twin interfaces in ZnO nanopikes have been reported, benefiting also from theoretical approaches developed for other wurtzite-type compounds (Yan *et al.*, 2005; Béré & Serra, 2003; Dai *et al.*, 2003; Ding & Wang, 2009). Moreover, experimental investigations on ZnO nanopikes have already demonstrated the presence of $(2\bar{1}\bar{1}1)^w$ domain boundaries separating the twin components (Huang *et al.*, 2008, 2009). For the present study, the emphasis was placed on a detailed investigation of the scattering and contrast phenomena produced by such superposition twinning of nanopikes. High-resolution transmission electron microscopy (HRTEM) and precession electron diffraction (PED) were applied, as these methods have proved to be excellent tools for investigating defect structures (Tomforde *et al.*, 2011; Kienle *et al.*, 2011). These advanced TEM methods enable the design of a comprehensive crystal model (Kienle & Simon, 2002), taking into account all relevant morphology and real structural features.

2. Experimental

2.1. Synthesis by the flame transport approach

ZnO nanopikes were prepared using the recently introduced flame transport synthesis (FTS; Kaps *et al.*, 2011), in which Zn microparticles with a typical diameter of 10 μm (Goodfellow, UK) are mixed homogeneously in an ethanol solution of polyvinyl butyral (PVB; Kuraray GmbH, Germany) powder. A typical weight ratio for Zn:PVB:ethanol is 1:2:6, but this can be varied depending upon the requirements for morphology and particular applications. The Zn–PVB–ethanol slurry is homogeneously coated onto Si substrates ($1 \times 1 \text{ cm}$) using a slip-casting technique and dried under ambient conditions. The Si substrates coated with the Zn–PVB–ethanol mixture are then heated inside a simple muffle-type box furnace to 873 K for 1 h with a ramp rate of 100 K min^{-1} . The main role of the PVB–ethanol blend is to act as a sacrificial spacing layer between the particles. At elevated temperatures the PVB decomposes completely, and ZnO nanopikes grow out of the Zn particles and establish a three-dimensional interconnected network of particle–spike structures. The length of the nanopikes can be varied from a few nanometres up to several micrometres by controlling the temperature and heating time.

2.2. Scanning electron microscopy

The morphological evolution of the synthesized particle–spike structures was analysed by scanning electron microscopy (SEM) using a Philips XL-30 microscope equipped with an LaB_6 filament and energy-dispersive detector for X-ray spectroscopy (EDX). SEM images of particle–spike structures were recorded at an electron beam acceleration voltage of 10 kV with a beam current of 15 μA .

2.3. Transmission electron microscopy

The specimens were ground and dispersed in *n*-butanol. One drop of the suspension was placed on a holey carbon/

copper grid. These grids were fixed in a side-entry double-tilt holder, with the tilting limited to a maximum of $\pm 25^\circ$ in two directions. HRTEM was carried out using a Philips CM 30 ST microscope (LaB_6 cathode, 300 kV, spherical aberration $C_s = 1.15 \text{ mm}$). A spinning star device enables the use of PED (Schürmann *et al.*, 2011; Vincent & Midgley, 1994) in addition to selected-area electron diffraction (SAED). Compared with SAED using stationary illumination, the movement of the beam on a precession cone (PED technique) is known to reduce dynamic scattering effects considerably. Thus, the so-called quasi-kinematic intensity is obtained in PED patterns after subsequent de-scanning. For the simulation of HRTEM micrographs and SAED and PED patterns, the software *EMAP*, the *JEMS* program package (Stadelmann, 1987) and the *xHREM* image-simulation program (Ishizuka & Uyeda, 1977) were applied using a multislice formalism (preferences: spread of defocus 70 Å, illumination semi-angle 1.2 mrad). Calculations of electron diffraction (ED) patterns with *EMAP* only consider single scattering events, while dynamic scattering effects were introduced via *xHREM*. All ED patterns and HRTEM micrographs were evaluated using the program *Digital Micrograph* (Version 3.6.1; Gatan Inc., California, USA). Chemical analyses by EDX were performed with an Si/Li detector (Thermo Fisher, Noran System Seven).

3. Results and discussion

3.1. Morphology

The morphology of the as-prepared ZnO particle–spikes obtained by the FTS approach is demonstrated by the SEM micrograph shown in Fig. 1(a). The nanopikes frequently appear as triangular flat rods of marginal thickness and a typical width below 1 μm (at the bottom), narrowing to several nanometres at the tip [cf. inset in Fig. 1(a)]. Chemical analyses via EDX in SEM and TEM prove the absence of any significant impurities within the ZnO nanopikes. The morphology of single nanopikes was characterized by TEM. The long axes of the nanopikes are always parallel to the $(1\bar{1}0\bar{1})^w$ edge. This strongly anisotropic crystal morphology leads to the preferred viewing direction along $[2\bar{1}\bar{1}3]^w$ (Huang *et al.*, 2008) when the crystals are dispersed on TEM grids [cf. sketch in Fig. 1(b)].

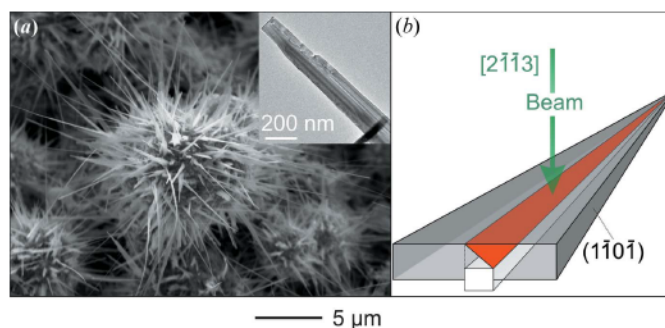


Figure 1
(a) A SEM micrograph of ZnO particle–spikes structures. Inset: Bright-field TEM image of a nanopike tip region along the zone axis $[2\bar{1}\bar{1}3]$. (b) An idealized scheme of a nanopike.

The scheme shown in Fig. 2 demonstrates theoretically the effect of superposition twinning on the contrast using simulated HRTEM micrographs. The two systematically oriented micrographs represent layers perpendicular to the preferred viewing direction $[2\bar{1}\bar{1}3]^w$ within each twin component. The domain boundary $(2\bar{1}\bar{1}1)^w$ propagates nearly parallel (reciprocal density of coincidence sites $\Sigma = 6$; Huang *et al.*, 2009) to the growth direction (*cf.* Fig. 2); however, the angle between the $[2\bar{1}\bar{1}3]^w$ direction and the normal of the domain boundaries is 47.5° (Otte & Crocker, 1965). Thus a superposition of the domains along the preferred viewing direction is produced, leading to a characteristic fringe contrast (Fig. 2, bottom; Huang *et al.*, 2008; Kaiser *et al.*, 1999). The subsequent discussion focuses on such superposition fringes and their quantitative interpretation. As a result of the morphology caused by the crystal growth such fringes are at least observable within selected areas of all HRTEM micrographs; however, the contrasts corresponding to the twin individuals were never observed in plane view on the same nanopike (see below). This finding indicates that the crystal model presented in Fig. 2 is strongly idealized. Obviously, the two twin individuals are not contributing equally, but one of them represents a major component while the minor component is attached to

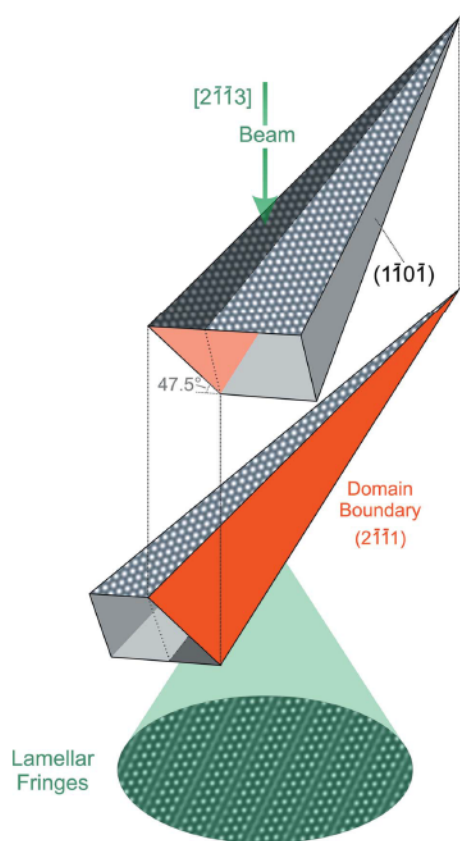


Figure 2

An idealized schematic model for the creation of fringe contrast by the superposition of twinned nanopikes (simulated micrographs for zone axis $[2\bar{1}\bar{1}3]^w$, thickness 3.68 nm, $\Delta f = -70$ nm). The domain boundary $(2\bar{1}\bar{1}1)^w$ is nearly parallel to the growth direction and is tilted with respect to the viewing direction by 47.5° , resulting in lamellar fringe contrast due to superposition.

the bottom/top surface of its twin [*cf.* sketch in Fig. 1(b)]. Wide-angle tilting experiments providing an edge-on view onto the twin boundary (cross section) would show no fringes. However, such experiments are complicated by the considerable increase of sample thickness expected in the course of tilting. Moreover, the tilt angle (47.5°) exceeds the maximum of $\pm 30^\circ$ for the applied microscope because of the confined space between sample holder and pole pieces. Another technique for avoiding the fringes would be cross-sectional TEM preparation and analysis, for example by focused ion beam milling or other dedicated techniques (Muller & Krumeich, 2000; Chen *et al.*, 2004; Vieweg *et al.*, 2012; Langford, 2006). First trials with focused ion beam milling point to considerable experimental problems interrelated with charging of the nanopikes, and thus the potential of the alternatives must be evaluated as the subject of a future project.

For the discussion of the experimental data, a representative wurtzite-type ZnO nanopike is shown in the bright-field TEM image of Fig. 3(a). Like all other examined nanopikes, the crystal appears to be subdivided into parts, with a sharp boundary occurring close to the centre and parallel to the axis of the nanopike [*cf.* arrows in Fig. 3(a)]. A magnified view of the area marked by the black square in Fig. 3(a) is depicted in

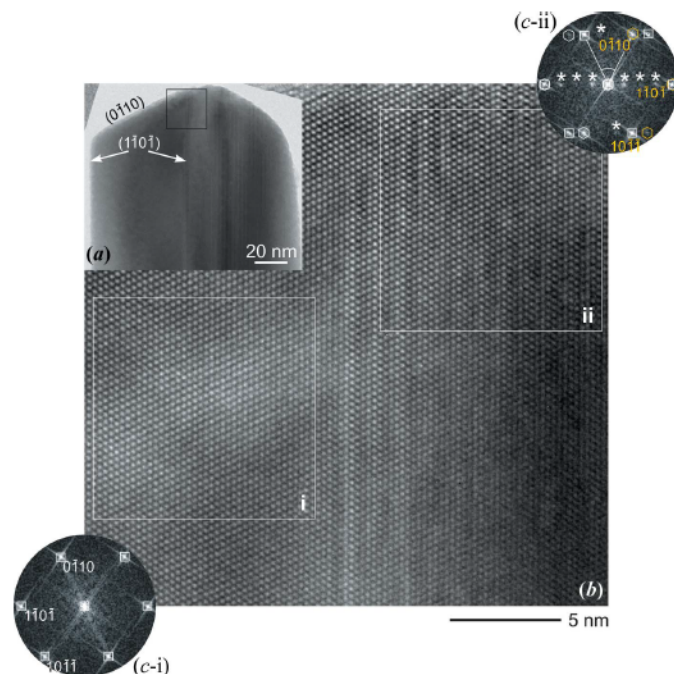


Figure 3

An experimentally investigated ZnO nanopike tip, with two separated areas exhibiting a simple spot pattern (area i) and lamellar fringes (area ii, fringe distance *ca* 1 nm) along the zone axis $[2\bar{1}\bar{1}3]^w$. (a) Bright-field TEM image. (b) HRTEM micrograph from the area marked in (a). (c) A comparison of the respective FFT patterns of areas i and ii. The marked intensities can be indexed by assuming two twinned wurtzite domains (hexagons and squares). Intensities marked with squares represent the majority twin component and those marked with hexagons the minority twin component. Multiple scattering effects (*i.e.* first-order satellites) are highlighted by asterisks. Experimental/literature (Sowa & Ahsbahs, 2006) values for the interplanar spacings (nm): $1\bar{1}0\bar{1}$ (0.248/0.24755), $10\bar{1}\bar{1}$ (0.248/0.24755), $0\bar{1}10$ (0.286/0.2814).

the high-resolution micrograph of Fig. 3(b). The highly crystalline structure of the nanospike tip is demonstrated. Two distinct contrast phenomena are present on opposite sides of the boundary in the HRTEM micrograph: area i with a periodic arrangement of bright spots, as expected from simulated micrographs for a single domain with wurtzite-type structure of ZnO (not shown, zone axis $[2\bar{1}\bar{1}3]^w$, objective lens defocus $\Delta f \simeq -70$ nm and a specimen thickness of 6.75 nm), and area ii with the spot pattern additionally showing fringes (fringe spacing *ca* 1 nm) parallel to the boundary. Further structural information is obtained by fast Fourier transform (FFT) analyses from the respective areas of the HRTEM micrograph. While the peaks in the FFT of area i (Fig. 3c-i) can be assigned to the single-domain structure, the FFT of area ii (Fig. 3c-ii) shows additional reflections. These reflections can be indexed by assuming a superposition of two single domains which could be mirrored at a plane parallel or perpendicular to $(1\bar{1}0\bar{1})^w$ [cf. the squares and hexagons in Fig. 3(c-ii)]. A complete indexing of the pattern in Fig. 3(c-ii) is presented in Table S T1 of the supplementary material.¹ Such a superposition can also be constructed by a rotation of two single-domain patterns around the common zone axis $[2\bar{1}\bar{1}3]^w$ [rotation angle 52.188° ; cf. angle marked in Fig. 3(c-ii)], as reported in previous work (Huang *et al.*, 2008). Note that the mirrored orientation of the single domains is not evident from HRTEM, since only one single domain is visible and the pattern is produced by the superposition of two domains. This finding reproduced on many crystallites indicates that one of the twin domains is forming a minority component with marginal volume fraction and irregular shape. Otherwise the mirrored contrast corresponding to the single domains could be identified at the opposite edges of the same nanospike. As a result of superposition, the FFTs and ED patterns contain high-intensity multiple scattering reflections (labelled in the following as 'satellite reflections'), appearing close to fundamental reflections [cf. intensities highlighted by asterisks in Fig. 3(c-ii)]. The effect of such multiple scattering was studied by applying Bragg filtering on FFTs calculated from selected areas. Thereby, two cases were compared: first, only fundamental reflections were considered [cf. marked spots in Fig. 3(c-ii)], and secondly, only the satellites. It became apparent that the satellites contribute to HRTEM observations by producing lamellar fringes, as illustrated in the supplementary material (Fig. S1). In order to rationalize the lamellar fringes seen in HRTEM a superposition structure (SPS) was constructed.

3.2. Model of the superposition structure

For the simulation of the SPS a supercell approach was applied, as reported for complex phases (Kienle & Simon, 2002; Deiseroth *et al.*, 2004). The supercell is constructed from the hexagonal unit cell of the wurtzite type; however, the metrics are optimized for implementation of the defect

structure. The experimental observations determine the computational model design, particularly the metrics of the supercell in the first step. In the present case the common zone axis $[2\bar{1}\bar{1}3]^w$ of the twin domains establishes one principal axis. Moreover, the approach should enable the implementation of the twin individuals in one common cell which restricts all angles to 90° . The cell has to contain all symmetry elements of the single-domain structure and the twin element, *i.e.* the mirror plane $(1\bar{1}0\bar{1})^w$. The supercell is set to a triclinic (*P1*) space group in order to avoid any symmetry restrictions; thus, all symmetry elements mentioned above represent pseudo-symmetry elements. All atoms in the SPS are crystallographically independent, and the manipulation of atom positions is straightforward. The construction procedure of the SPS model splits into three separate steps.

(1) The coincidence of main viewing direction $[2\bar{1}\bar{1}3]^w$ and a principal axis of the supercell is required. Therefore, the symmetry of the wurtzite-type structure is reduced in two steps from *P6₃mc* to the t-subgroups *Cmc2₁* (*a*, *a* + 2*b*, *c*) and subsequently to *Cc* (*a*, *b*, *c*, $\beta = 90^\circ$). This transformation adopts the zone axis $[2\bar{1}\bar{1}3]^w$ as principal axis.

(2) By rotation of the *Cc* structure around $[2\bar{1}\bar{1}3]^w$, one of the principal faces of the supercell is aligned parallel to the plane $(1\bar{1}0\bar{1})^w$. In this step a rectangular supercell is required for the realization of the third step. The larger the distortions from rectangularity, the larger will be the error in the atomic positions of the superposition structure. Thus, only the slightest deviations ($<<1^\circ$) are acceptable for the respective angles. In order to meet these criteria, a two-step transformation of the *Cc* structure was applied: firstly to an intermediate triclinic model (lattice parameters *a* = 3.249, *b* = 5.627, *c* = 6.138 Å, $\alpha = 90$, $\beta = 121.96$, $\gamma = 90^\circ$) by applying the

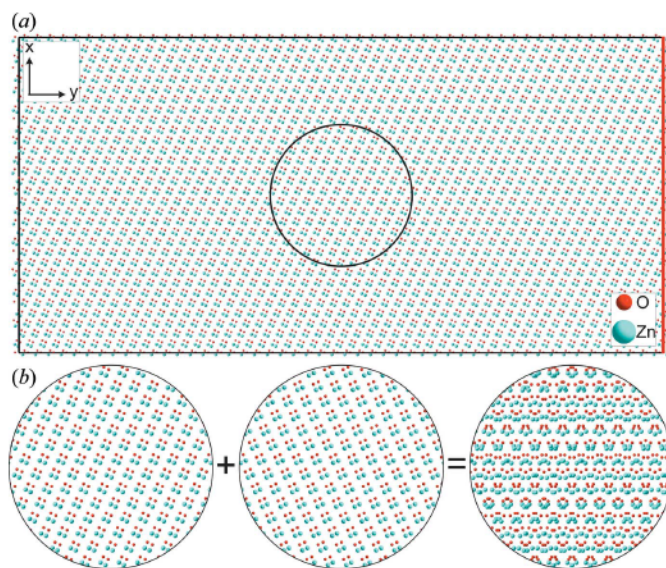


Figure 4

The supercell approach for the wurtzite-type ZnO nanospikes along the $[2\bar{1}\bar{1}3]^w$ projection. (a) The rectangular cell resulting from transformation step (2). The vertical line on the far right (shown in red in the electronic version of the journal) shows the alignment of the $\{010\}^{\text{Supercell}}$ plane. (b) Enlarged area of the structure inside the supercell (left), its mirror image (centre) and the superposition (right).

¹ Supplementary material is available from the IUCr electronic archives (Reference: KS5331). Services for accessing this material are described at the back of the journal.

matrices P and Q , respectively [transformation conventions refer to Hahn (2002)],

$$P = \begin{pmatrix} 25 & 0 & 7 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad P^T = \begin{pmatrix} 25 & 0 & 0 \\ 0 & 1 & 0 \\ 7 & 0 & 1 \end{pmatrix}, \quad (1)$$

$$Q^T = \begin{pmatrix} 1/25 & 0 & 0 \\ 0 & 1 & 0 \\ -7/25 & 0 & 1 \end{pmatrix},$$

and secondly to the final triclinic and rectangular $P1$ supercell (cf. Fig. 4a; lattice parameters $a = 76.74$, $b = 156.7$, $c = 6.138$ Å, $\alpha = 90.01$, $\beta = 90.02$, $\gamma = 90^\circ$) via

$$P = \begin{pmatrix} 1 & 6 & 0 \\ 1 & -25 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad P^T = \begin{pmatrix} 1 & 1 & 0 \\ 6 & -25 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (2)$$

$$Q^T = \begin{pmatrix} 25/31 & 1/31 & 0 \\ 6/31 & -1/31 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Maintaining rectangularity, the twinning can be introduced easily. The SPS is generated by adding the atomic coordinates of two structures, namely the one obtained in step (2) and the mirrored one by inversion of the y parameter [*i.e.* applying a mirror plane at $(010)^{\text{SPS}}$ as illustrated in Fig. 4(b)]. Thus, the number of atoms with respect to the triclinic supercell of

Fig. 4(a) is doubled, resulting in a total number of 12 000 atoms. A comparison of the supercell and the SPS is presented in the supporting material (Fig. S2).

3.3. Dynamical simulation of the diffraction patterns

The resulting SPS allows the calculation of kinematic intensity and multiple scattering phenomena, which can be used to interpret the experimentally obtained PED patterns. In Figs. 5(a), 5(c) and 5(d), simulated diffraction patterns assuming increasing specimen thickness are depicted and compared with an experimental PED pattern. In Fig. 5(a) multiple scattering is excluded for the simulation, resulting in a purely kinematical diffraction pattern. Hence, a comparison of the kinematical simulation with the experimental data of Fig. 5(b) allows a direct identification of dynamical contributions in terms of additional experimentally observed reflections. A multislice algorithm is applied for illustrating more explicitly the multiple scattering. Even for low sample thickness (2.46 nm; Fig. 5c), dynamical intensity is significantly excited (cf. marked reflection). A further increase of the sample thickness for the simulations led to the appearance of even more reflections, including higher-order satellites, as shown in Fig. 5(d). Comparing the simulations with the experimental pattern, a better match is achieved by considering dynamical effects and keeping the specimen thickness low. Indeed a low specimen thickness is verified experimentally by the strong intensity of the primary beam (cf. Fig. 5b), which can only originate from a low interaction of the electron beam with the specimen. However, it became apparent that the thickness is not the only decisive parameter for the interpretation of the diffraction phenomena: the twin component ratio is also important (cf. discussion in §3.4).

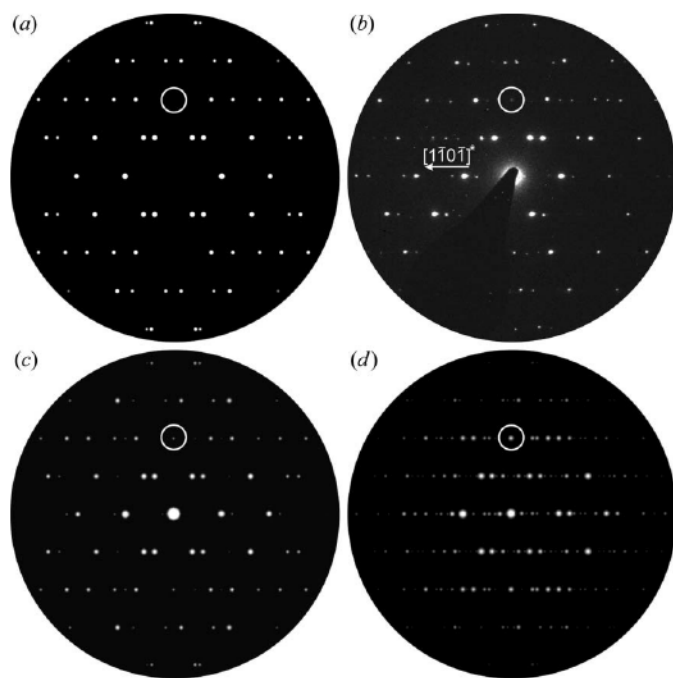


Figure 5

Experimental and simulated PED patterns for twinned ZnO along zone axis $[2\bar{1}\bar{1}3]^*$, using a twin component ratio of 1:1 for the simulations. (a) Kinematic simulation *versus* (b) experimental pattern. (c) and (d) Simulated PED patterns based on specimen thicknesses of (c) 2.46 nm and (d) 6.14 nm, illustrating multiple scattering effects by the occurrence of satellite reflections.

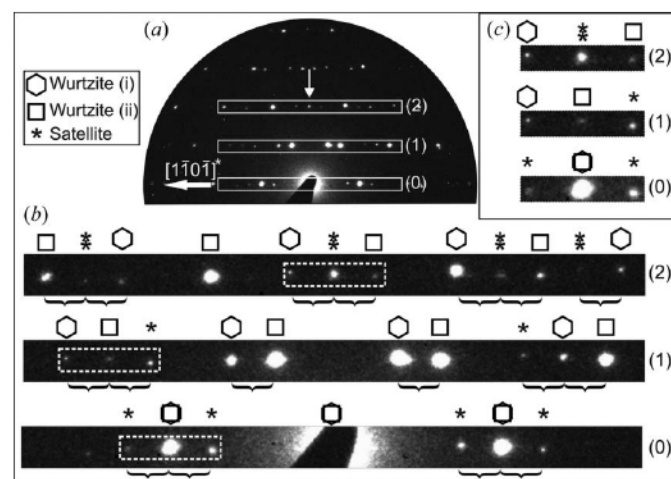


Figure 6

(a) Experimental PED pattern of the twinned ZnO structure along the $[2\bar{1}\bar{1}3]^*$ zone axis. (b) Enlarged view of rows of reflections (0, 1 and 2) parallel to the $[1\bar{1}0\bar{1}]^*$ direction. Hexagons and squares denote reflections of each wurtzite domain, and asterisks denote the first-order satellites of the twin pattern. The repeat distance between reflections is marked with downward pointing brackets. (c) Reflection triplets (dashed boxes) of the respective rows, with variable origin.

Three systematic rows of reflections 012 parallel to $[1\bar{1}0\bar{1}]^*$ were investigated in detail, as depicted in Fig. 6. According to the single-domain ZnO structure along the zone axis $[2\bar{1}\bar{1}3]^w$, the reflections marked with squares and hexagons (cf. Fig. 6b) can be assigned to the kinematic contributions of the individual twin components. These main structure intensities show repeating peak-to-peak distances of *ca* 4.12 nm^{-1} (marked with downward pointing brackets) for each domain. Moreover, all systematic rows contain first-order satellite reflections at a distance of 1.0 nm^{-1} . According to the superposition each row is characterized by reflection triplets [cf. enlarged sections in Fig. 6(c)] centred on coinciding main structure reflections (row 0), separated main structure reflections (row 1) and coinciding first-order satellites (row 2). The first-order satellite reflection marked by an arrow (Figs. 6a and 6b, top) becomes a noticeable feature as a result of its strong intensity. The adjacent main structure intensities $(\bar{1}\bar{1}21)^w$ and $(\bar{1}\bar{1}21)^w$ are kinematically forbidden by violating the zonal reflection condition $h h \bar{2} h l: l = 2n$ according to the wurtzite-type structure. Thus, the strong intensity of the satellite reflection could be a result of the dynamical contributions from both main structure reflections to the same extent (cf. Fig. 6c). A complete indexing of the experimental PED pattern of Fig. 6 is provided in the supplementary material in Table S T2.

Furthermore, a comparative study of PED and SAED patterns recorded on the same selected area shows remarkable differences when these are recorded directly next to the boundary separating a single domain and a superposition area of the twin individuals. In contrast to the expected reduction of multiple scattering effects by superposition in PED *versus* SAED mode, satellite intensities are displayed with enhanced intensity in the PED pattern (cf. Fig. S3 in the supplementary material). The comparison also demonstrates that the kinematic contributions of the second component are enhanced in PED. Thus, the enhancement of multiple scattering stems from the different transmitted crystal volumes in SAED and PED. For the latter, an enhanced transmitted volume is expected as a result of beam precession, thus exciting the kinematic and multiple scattering effects arising from the minor twin individual.

3.4. Simulation of high-resolution contrasts and Fourier transforms

Considering a variable three-dimensional shape of the superimposed domains, different volume fractions and thus twin component ratios might contribute to the resulting TEM image. Therefore, the twin component ratio is introduced as a parameter for the simulation. To account for the parameter in the SPS, the occupancy factors of each atom are adjusted according to the twin component ratio. The total values for both domains are restricted to one. For the simulation and interpretation of the HRTEM micrographs this ratio plays a decisive role. As expected and frequently observed, at the thin areas of the tip and at the edges of the nanospike, the amount of one single component is significantly enhanced. Thus, the characteristic stripe contrast resulting from superposition is

not significant in these areas. In Fig. 7(a) the influence of the twin component ratio is sketched for the SPS (zone axis $[2\bar{1}\bar{1}3]^w$). The simulations shown in Figs. 7(b) and 7(c) are based on ratios of 1:4 and 1:1, respectively. Assuming Scherzer focus conditions and the weak phase object approximation, the projected potential (Fig. 7b) correlates with the HRTEM contrast [cf. simulated micrographs depicted in Fig. 7(c)]. Note that because of the limitations in resolution ($d_{\text{Scherzer}} = 0.19\text{ nm}$) closely spaced atoms are condensed to one dark spot. Apparently, the variation of the twin component ratio determines the HRTEM contrast. In particular, the marked regions exhibit considerable changes by switching the dark spots from a rhomboidal to a rectangular arrangement. The reason can be seen in the corresponding projected potentials. The potential for the 1:4 ratio (Fig. 7b, top) shows strong contributions for only one component. Thus, the HRTEM contrasts do not show strong deviations from the image of the single-domain structure, namely the rhomboidal arrangement of dark spots. By increasing the ratio to 1:1 (Fig. 7b, bottom) a square arrangement of the dark contrast spots is produced, as also expected from enhanced contributions of both twin components to the projected potential (Fig. 7c, bottom).

Another parameter for the HRTEM simulations can be an additional shift of the twin components relative to each other (Béré & Serra, 2003; Kienle *et al.*, 2011; Deiseroth *et al.*, 2004). Since the Fourier transform is invariant towards translation, electron diffraction is not affected. In order to probe for a shift the x and y coordinates of one twin individual within the SPS were changed. Thereby, a series of simulations validated that changes of the y coordinates (*i.e.* shift parallel to the fringes) give only slight variations of the simulated HRTEM contrast. A close inspection of different SPSs each based on different y coordinates indicates that highly related atomic arrangements are produced, which cannot be discerned within the resolution limit of the microscope.

In contrast, variations of the x coordinates result in significant changes of the HRTEM contrast. However, the simulations demonstrated that an additional shift of the x parameters

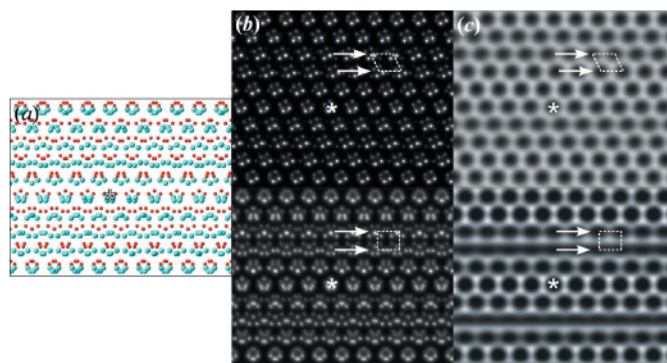


Figure 7
Simulated results, showing the influence of a variation in the twin-component ratio on HRTEM contrast along the $[2\bar{1}\bar{1}3]$ zone axis. (a) A cut-out of the SPS. (b) and (c) (Top) A 1:4 and (bottom) a 1:1 ratio for the twin components compared for (b) the projected potential and (c) the resulting high-resolution contrast close to the Scherzer focus ($\Delta f = -56\text{ nm}$) for a thickness of 3.65 nm . The asterisks mark the same position within the respective images.

does not improve the agreement between the experimental and simulated HRTEM contrasts. Thus, the final model for contrast interpretation contains no shift of the x parameter. A comparison of experimental and simulated HRTEM contrast is depicted in Fig. 8 for underfocus imaging conditions, $\Delta f = -80$ nm (Fig. 8a) and $\Delta f = -56$ nm (Scherzer focus; Fig. 8b). Experimental and simulated HRTEM micrographs show complementary black and white contrast in the course of defocusing. This effect is enhanced by Bragg filtering, as shown in Figs. 8(c) and 8(d). The simulations in Figs. 8(c) and 8(d) (cf. insets, twin component ratio 1:4) convincingly agree with the experimental images.

The influence of the twin component ratio is also represented in the comparison of experimental and simulated FFTs. In Fig. 9(a) the FFT pattern of area ii in Fig. 3 is depicted, along with calculated FFTs from circular regions of simulated HRTEM micrographs of a 1:4 (Fig. 9b) and 1:1 ratio (Fig. 9c). Apparently, the experimental data show a high asymmetry with respect to the peak intensities and not the mm symmetry calculated for a 1:1 ratio. On changing the ratio to 1:4, a comparable mismatch between the main structure intensities

appears, resulting in a better agreement between experiment and simulation.

4. Summary and conclusions

In this work, electron microscopy has been applied for the investigation of one-dimensional ZnO nanospikes, which show intrinsic twinning as the main real structural feature. As a result of the specific morphology of these spikes, a preferential viewing direction along $[2\bar{1}\bar{1}3]^w$ is predetermined, forcing superposition of the twin domains with respect to the electron beam. An SPS allowed the simulation of all experimentally observed features, based on the superposition, particularly the fringe contrast in HRTEM and multiple scattering phenomena observed in electron diffraction patterns. The mode of electron diffraction strongly influences the intensities of the satellite reflections. Owing to the differently transmitted volumes, their intensity is enhanced in PED patterns recorded next to a fringe boundary. A strong influence of the twin component ratio on the contrast has been demonstrated, indicating that the twinned crystals are strongly dominated by one component. These results are supported by the comparison of experimentally obtained images with calculated high-resolution micrographs and Fourier transformations.

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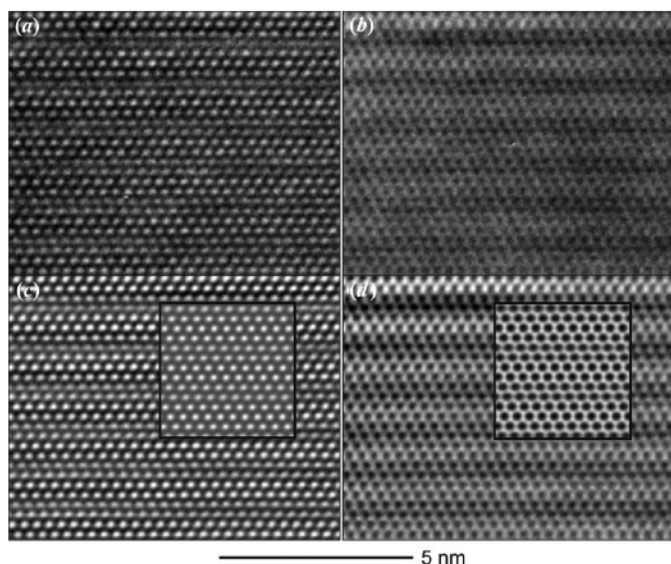


Figure 8
Experimentally obtained HRTEM micrographs with different defocus values, (a) $\Delta f = -80$ nm and (b) $\Delta f = -56$ nm, and a thickness of 3.65 nm in zone axis $[2\bar{1}\bar{1}3]^w$. (c) and (d) The respective Bragg-filtered HRTEM micrographs with inserted simulations.

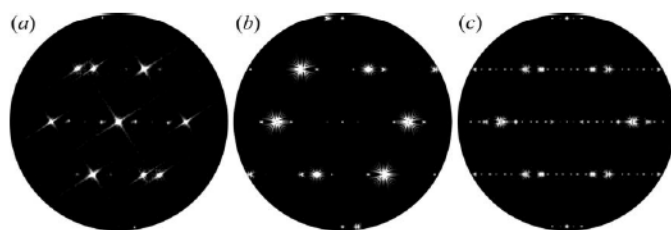


Figure 9
Comparison of (a) an experimentally obtained FFT, and (b) and (c) simulated FFTs with a focus value $\Delta f = -70$ nm and a specimen thickness of 6.75 nm in zone axis $[2\bar{1}\bar{1}3]^w$ for a component ratio of (b) 1:4 and (c) 1:1.

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