Inversion boundary induced grain growth in ZnO ceramics: from atomic-scale investigations to microstructural engineering

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Abstract. In semiconducting materials special boundaries play the key role in crystal growth. They introduce an abrupt structural and chemical anisotropy, which is readily reflected in an unusual microstructure evolution, whereas their local structure affects the physical properties of semiconducting materials. These effects, however, can be exploited to tailor the electronic and optical properties of the materials, as demonstrated in this review. The presented topic fits in the field of preparatory stage of phase transformations, manifested through evolution of chemically induced structural faults. In the noncentrosymmetric structure of ZnO, inversion boundaries (IBs) are the most common type of planar faults that can be triggered by the addition of specific spinel-forming dopants (Sb$_2$O$_3$, SnO$_2$, TiO$_2$). In addition to conventional HRTEM techniques several new methods were developed to resolve crystallography and atomic-scale chemistry of IBs. The absolute orientation of the polar c-axes on both sides of the IB was determined by a novel quantitative microdiffraction method, providing a reliable identification of crystal polarity in noncentrosymmetric crystals. To determine sub-monolayer quantities of dopants on the IB, we developed a special technique of analytical electron microscopy using concentric electron probe (CEP) in EDS or EELS mode, providing more accurate and precise results than any other available technique. Knowing the local crystal chemistry of IBs we were able to design experiments to identify their formation mechanism. IBs nucleate in the early stage of grain growth as a dopant-rich topotaxial 2D reaction product on Zn-terminated surfaces of ZnO grains. Soon after their nucleation, ZnO is epitaxially grown on the inherent 2D phase in an inverted orientation, which effectively starts to dictate anisotropic growth of the infected crystallite. In very short time the grains with IBs dominate the entire microstructure in ZnO ceramics via IB-induced exaggerated grain growth mechanism. This phenomenon was used to design physical properties of ZnO-based varistor ceramics, whereas the bottom-up approach demonstrated here provides the basic tool for microstructural engineering of functional materials in virtually any system that is prone to formation of special boundaries.
1. ZnO-based varistor ceramics

Varistors are electronic components with highly nonlinear dependency between current ($I$) and voltage ($U$), therefore they are widely used for surge protection of electronic circuits and devices:

$$ I = K \cdot U^\alpha $$

(Eq. 1)

The coefficient $\alpha$ is a measure of the varistor's nonlinearity and its value in a commercial varistor is in the range from 30 to 80 [1]. A typical varistor $U$-$I$ curve is shown in Figure 1a.

![Figure 1](image)

**Figure 1:** (a) Typical varistor curve showing the characteristic $U$-$I$ dependence. Each ZnO-ZnO GB presents a charge barrier of ~3.5 V. The total breakdown voltage of the varistor depends on the number of active GBs between the two electrodes: (b) fine-grained microstructure for high-voltage applications and (c) coarse-grained microstructure for low-voltage applications.

The basic function of the protection device is that it acts as a resistor until the nominal breakdown voltage is reached, above this threshold, however, it suddenly (in nanoseconds) becomes orders of magnitude more conductive than the electronic device it protects. This quick response enables the surge voltage to be transferred through the varistor and prevents damage to the electronic device. Nowadays the vast majority of varistors is based on semiconducting zinc oxide (ZnO) ceramics sintered with various metal oxide additives in order to enhance the varistor's electrical properties. An ideal varistor is composed of highly conductive uniformly sized ZnO grains, separated by highly non-conductive nonlinear varistor-type grain boundaries (GBs), which produce the so-called varistor effect. In a varistor, an active ZnO-ZnO GB acts as a single switching device (diode) with a switch (or breakdown) voltage of about 3.5 V [1]. The most common additive that produces thin resistive GB layers in ZnO varistors is bismuth oxide (Bi$_2$O$_3$). During sintering the Bi-rich liquid phase distributes evenly along the GBs, where it forms a thin charge-barrier layer after solidification [2]. High GB resistivity defines the varistor's performance in the pre-breakdown region, where it conducts only a negligible leakage current. This unwanted effect mainly depends on the amount of secondary phases and non-resistive GBs [3]. The overall breakdown voltage of the varistor depends on the effective number of active GBs between the electrodes. As soon as this nominal voltage is surpassed the conductivity of ZnO grains becomes essential. To increase the conductivity of ZnO grains transition metal oxides (Mn, Ni, Cr, etc.) are added [4]. One of the major parameters for production of varistors for diverse voltage applications is therefore the number of active GBs. This can be simply controlled by the size...
of ZnO grains. In principle, varistors with smaller average grain size are implemented for high-voltage applications, whereas those with larger average grain size are used for low-voltage applications (Figs. 1b and 1c). ZnO grain size is controlled by a group of dopants (i.e. Sb$_2$O$_3$, SnO$_2$, TiO$_2$, etc.), which are called grain-growth modifiers due to their influence on ZnO microstructure development [4-8].

2. The role of dopants in ZnO-based varistor ceramics

Grain size control in ZnO varistor ceramics is quite challenging because commercial varistor compositions contain many interdependent dopants, which were empirically added to achieve the required electrical properties. Besides their influence on electrical properties, each dopant also influences ZnO grain growth. The grain growth is therefore not simply influenced by the initial grain size of ZnO and the additives and their recrystallization within the specific processing regime, but also by the formation of their reaction products in the various stages of sintering [9]. To make things even more complicated, different molar ratios of the dopants, for example, that between Bi$_2$O$_3$ and Sb$_2$O$_3$, lead to diverse reaction pathways during sintering, which all in their own way influence ZnO grain growth.

In order to understand the influence of individual additives their role in ZnO grain growth must be investigated. Sintering of pure ZnO is controlled by solid-state diffusion [10]. In the presence of Bi$_2$O$_3$, sintering of ZnO becomes liquid-phase assisted. Bi$_2$O$_3$ melts at 740°C (ZnO-Bi$_2$O$_3$ eutectic) enhancing the densification of the sample, whereas the ZnO grain growth rate depends on the amount of Bi$_2$O$_3$ addition. At very low additions (<0.05 mol%), ZnO grains that are in contact with Bi$_2$O$_3$ grow exaggeratedly due to partial wetting [2]. At moderate additions of Bi$_2$O$_3$ (0.05-1 mol%), the liquid phase present at every GB enhances the diffusion process and hence ZnO grains grow rapidly according to a solution-precipitation phase-boundary reaction mechanism [10]. Higher additions of Bi$_2$O$_3$ (>1 mol%) however, cause diffusion paths through Bi$_2$O$_3$ liquid phase to become longer and consequently ZnO grain growth is slowed down [11]. Typical additions of Bi$_2$O$_3$ in varistor compositions are about 1 mol%. In order to more efficiently control the ZnO grain size, other dopants are added to the binary ZnO-Bi$_2$O$_3$ varistor composition. The most common grain growth controlling additives for ZnO-based varistor ceramics are Sb$_2$O$_3$, SnO$_2$ and TiO$_2$ [4-8]. Empirically, Sb$_2$O$_3$ would be added when small ZnO grain size is desired, while the addition of TiO$_2$ generally results in large-grained microstructure.

Typical microstructures of high- and low-voltage ZnO-based varistor ceramics are shown in Figure 2. In spite of an obvious difference between the final microstructures, there has been a lot of dispute in what way these additives actually influence the ZnO grain growth. Popular explanations rely on the so-called particle pinning mechanism, based on Zener’s drag phenomenon, which should act as an inhibiting force working against the ZnO grain growth [12]. This explanation was supported by the fact that adding higher concentrations of grain growth controlling additives (typically Sb$_2$O$_3$) resulted in the formation of more spinel grains [5,6]. As with the increasing concentration of spinel grains also the ZnO grain size becomes smaller, the spinels were consequently held responsible for inhibited ZnO grain growth. While this phenomenological correlation generally appears to be true, it fails to explain exaggerated grain growth in TiO$_2$-doped varistor ceramics [7], where despite an abundant presence of spinel grains some ZnO grains grow swiftly, disregarding any (spinel) particle pinning force that might be acting on the course of rapidly expanding ZnO grains. In addition to spinels, the grain growth controlling additives also cause the formation of IBs in ZnO grains. Their possible influence on ZnO grain growth was ignored until first TEM studies showed that spinel-forming dopants are present on IBs and made a clear connection that they are a consequence of the addition of grain growth controlling additives [13,14]. Soon IBs were suspected to have certain influence on grain growth, although their actual role was not truly understood: in TiO$_2$-doped varistor ceramics, for example, IBs were held responsible for exaggerated grain growth [7], while in Sb$_2$O$_3$-doped ceramics they were deemed to have an inhibiting effect on ZnO grain growth [5,6]. In our investigations we focused on evaluation of these effects on microstructure development in ZnO-based varistor ceramics.
Figure 2: Typical microstructures of ZnO-based varistor ceramics: (a) high-voltage varistor ceramics with fine-grained microstructure - grain growth is inhibited due to (spinel) particle pinning mechanism (dopants: Sb$_2$O$_3$ and SnO$_2$). (b) Low-voltage varistor ceramics with coarse-grained microstructure - exaggerated grain growth is caused by the presence of IBs in some ZnO grains (TiO$_2$-doping). Spinel particles are overgrown.

3. Microstructure development in SnO$_2$-doped ZnO-Bi$_2$O$_3$ ceramics

To understand the role of grain growth modifying additives in the ZnO grain growth, basic ZnO-Bi$_2$O$_3$ varistor composition was doped with SnO$_2$ [8]. While the addition of SnO$_2$ to varistor ceramics is not favourable for the electric properties of the ZnO-based varistor, because it increases the leakage current [15], it turned out to be a perfect dopant for the grain growth mechanisms studies. Surprisingly we observed that adding very small amounts of SnO$_2$ to the basic varistor composition resulted in unexpected coarse-grained microstructure. The addition of even the lowest amounts of SnO$_2$ triggers formation of spinel particles and if the particle pinning mechanism was controlling the grain growth, the size of ZnO grains should be smaller than that in the dopant-free microstructure even at the lowest additions of the spinel forming dopant. But this was not the case. ZnO grains sintered with 0.1 mol% of SnO$_2$ were almost twice as large as the ZnO grains sintered without the spinel forming dopant. With the increasing concentration of SnO$_2$ the ZnO grain size was gradually reduced so that between 0.5-2.0 mol% of SnO$_2$ addition the ZnO grain size reached the grain size of undoped ZnO! This unusual behaviour shed a serious doubt on the popular explanation of grain growth inhibition by the presence of spinel particles. In all microstructures spinel grains were regularly present, but they did not present any obstacle for ZnO grain growth. Only at very high additions of SnO$_2$ the ZnO grain size became much smaller than that in normal ZnO without SnO$_2$ (Figure 3). We could confirm that with the increasing SnO$_2$ addition ZnO grain size was decreased, but the large initial increase of ZnO grain size at low SnO$_2$ additions could not be explained by any known grain growth mechanism.
Figure 3. A sequence of microstructures starting from undoped ZnO, ZnO doped with 1 mol% of Bi$_2$O$_3$, and those with different additions of SnO$_2$. The grain sizes of undoped ZnO ($D_0$) and that with Bi$_2$O$_3$ addition are comparable ($D\approx D_0$). As soon as SnO$_2$ is added to this composition the grain size is surprisingly increased by a factor of 2 ($D\gg D_0$). With increasing SnO$_2$ addition ZnO slowly reaches the average grain size of undoped ZnO ($D_0$) and only at above 10% addition of SnO$_2$ the grain size is reduced by about a factor of 2 if compared with normal ZnO grain size ($D\ll D_0$).

To explain this unusual increase in ZnO grain size with small additions of SnO$_2$ we investigated the early stages of ZnO grain growth [8]. Along with spinel particles the addition of spinel forming dopant triggers the formation of IBs in ZnO grains. The influence of these planar defects on microstructure development was not studied before. At the beginning of grain growth IBs form in some ZnO grains. These grains are nuclei for anisotropic grain growth. In the samples with larger SnO$_2$ additions, more nuclei are formed, whereas in the samples with lower SnO$_2$ additions the number of nuclei is comparatively smaller. As the growth proceeds these grains grow faster than normal ZnO grains. The growth of such crystallite is controlled by the growth of an inherent planar fault. This grain growth mechanism was called IB-induced grain growth. Following this mechanism grains with IBs grow preferentially in the direction parallel to the inherent IB plane and may reach unusually high aspect ratios. Resulting grains become highly anisotropic. When the longer axes of elongated grains reach lengths equal to the mean free distance between the grains with IBs, their anisotropic growth is stopped. If we have more nuclei the collisions occur sooner, and the resulting grains are smaller. After this stage another growth mechanism prevails, causing the elongated grains to thicken. This stage is to be compared with seed growth where according to the Ostwald’s ripening Law grains with larger curvature radii grow at the expense of the surrounding smaller grains. ZnO grains with IBs grow exaggeratedly at the expense of normal ZnO grains until they entirely dominate the microstructure. The final microstructure is thus composed of only ZnO grains with IBs. The average size of the grains in the final microstructure equals the mean free distance between the IB nuclei, and is inversely proportional to the amount of spinel forming dopant added to the basic ZnO composition. Now the sudden increase of ZnO grain size on low additions of spinel forming dopant can be explained. Low addition of SnO$_2$ produces only a small number of IB nuclei and the resulting microstructure would be coarse-grained, whereas larger amount of SnO$_2$ would produce a large number of IB nuclei and result in fine-grained microstructure. Higher levels of SnO$_2$ addition also lead to increasing amount of secondary phases, however, their influence on ZnO grain growth is subordinated to the role of IBs [8].

In order to fully understand the nature of IBs and their true influence on ZnO grain growth, we performed a complete top-down chemical and structural analysis of these planar faults.
4. Atomic structure of inversion boundaries

The atomic structure and the chemistry of IBs in Sb$_2$O$_3$-doped ZnO were investigated by quantitative TEM techniques. Convergent beam electron diffraction (CBED) and high-resolution TEM (HRTEM) methods were used to determine the orientation of the polar c-axis on both sides of the inversion boundary and the translation state between the inverted ZnO domains. Quantitative energy-dispersive X-ray spectroscopy (EDS) combined with HRTEM analysis allowed us to determine the exact amount and the arrangement of Sb in the boundary layer. IBs were found to be head-to-head oriented, and the IB plane consists of a highly ordered SbZn$_3$ monolayer where the cations occupy octahedral interstices of the structure. In the octahedral boundary layer, Zn and Sb atoms constitute a honeycomb superstructure with a three-fold (3m) in-plane symmetry [16]. Both, the inversion as well as the composition of IBs have long reaching influence on physical properties and grain growth of ZnO.

4.1. Crystallography of IBs in ZnO

The orientation of the polar c-axis across the IB plane is considered the most important feature that must be determined to characterize the translational state of an interface in non-centrosymmetric crystals. As shown in our early study on Sn-rich IBs in ZnO simple chemical etching of polished microstructures including ZnO grains with IBs indicates an inversion of the polar c-axis across the IB plane by the reversal of triangular etch-pits in adjacent crystal domains [8]. In order to prove the inversion on the structural level we developed a new technique, which allows determination of polar axes in non-centrosymmetric crystals by a simple electron diffraction method in TEM [17,18]. The so-called micro-diffraction technique is based on the fact that due to the breakdown of the Friedel's Law the scattering factors for g and -g reflections are different in non-centrosymmetric structures. Based on semi-kinematic interactions between zero-order Laue zone reflections we showed that the absolute orientation of the c-axis could be obtained already from very thin crystals. The difference can be observed under convergent beam electron diffraction (CBED) conditions, using a small condenser aperture to avoid overlapping of the diffraction disks. The crystal polarity can then be simply deduced from the intensity of the diffraction disks. By comparing the computed and experimental micro-diffraction patterns we demonstrated that the polar c-axes of the two crystal domains are oriented towards the interfacial plane to form IBs in head-to-head (→) configuration (Figure 4).

The fact that IBs in Sb$_2$O$_3$-doped ZnO are head-to-head oriented is not only important for understanding the crystallography of these planar faults, but has far reaching implications related to electronic charge transport through the polycrystalline material. Namely, if a perfect ZnO crystal starts with an O layer and terminates with a Zn layer, then the electroneutrality of the crystal is retained. By the inversion, Zn atoms in the inverted crystal domain are shifted from type-I to type-II tetrahedral sites across the IB plane. This translation produces a new O-terminating layer on the other end of the crystal that was Zn-terminated prior to inversion, while the charge surplus is balanced in the IB layer. Duplication of O-terminating planes should markedly increase the current-voltage barrier at the ZnO grain boundaries. This alone would, in effect, improve the non-linear varistor characteristics. This aspect of surface-charge transport caused by the inversion of ZnO crystals [19] has not yet been studied in the scientific literature. These two effects, (i) the increased current-voltage barrier at the surface of the ZnO grains caused by a head-to-head inversion and, (ii) the internal barrier caused by the presence of IB layer, should not be present in ZnO ceramics without IBs. A supporting evidence for such effect can be seen in empirical α-values of varistor ceramics with or without Sb$_2$O$_3$ doping. Namely, comparable varistor compositions with Sb$_2$O$_3$ addition display twice as high α-value compared to crystals of that composition without this dopant [4]. Now that we know that Sb$_2$O$_3$ triggers formation of IBs in every ZnO grain this increase in α-value can be explained by the above mechanism.
Figure 4. Inversion of crystal domains is revealed already by etching, where the orientation of the etch-pits is reversed across the IB (SEM). Micro-diffraction patterns are recorded on both sides of the basal-plane IB in ZnO crystal oriented along the [21\-10] zone axis (TEM). Pairs of reflections not related to the mirror plane show different intensities and the patterns on both sides of the IB are inverted. Calculated intensities of these reflection pairs indicate a head-to-head (→\←) orientation of the adjacent ZnO domains across the IB.

Translational state of coherent basal-plane IBs was investigated by quantitative HRTEM. The reversal of the c-axis and an apparent lattice dilatation across IBs allowed us to distinguish these faults from basal-plane SFs, which are rather common in ZnO. HRTEM images in [2\1\10] projection revealed a rigid-body shift of $\frac{1}{3}[0\1\10]$, whereas in the [0\1\10] projection no shift was observed, resulting in total displacement vector of $R_{IB} = \frac{1}{3}[0\1\10] - \Delta[0001]$. This shift is identical to a displacement observed on basal-plane SFs, which is produced in a wurtzite lattice by a 180° rotation of (0002) layer into (faulted) cubic stacking. The SF shift is followed by inversion operation where Zn\textsuperscript{2+} ions are shifted from type-I to type-II tetrahedral sites across the fault plane to produce an IB. The basal plane displacement depends on the type of the dopant and its oxidation state that due to local repulsion forces produce a rigid block relaxation $\Delta$. In Sb-rich IBs the $\Delta = 0.102$ was measured by quantitative HRTEM analysis [16]. Another very prominent feature that could be observed from HRTEM images is dopant ordering in the IB-layer implying the occupancy of either 1/3 or 2/3 of Sb atoms in the IB plane (Figure 6 [16]).

4.2. Chemical composition of IBs in ZnO

The exact chemical composition of IBs is one of the most important parameters for determination of the interface structure. The very first analyses of the IB plane involved a spatial-difference technique [13]. This method is based on acquiring one EDS/EELS spectrum on the interface of interest and another in bulk crystal. The amount of the dopant on the interface is obtained by the difference between the two spectra. Spatial difference EDS analysis of Sb-rich IBs in ZnO [13] indicated that 1.0 ± 0.5 monolayer of Sb is uniformly distributed in the IB plane. With spatial difference technique it is fairly impossible to accurately determine the specimen thickness, which leads to high systematic errors of such measurements. This technique therefore does not provide a sufficient accuracy that would allow a
distinction between the two possible Sb arrangements (1/3 or 2/3) in the IB plane. To solve such problems a new analytical method for measuring small amounts of dopants at interfaces was designed.

**Figure 5.** Schematic presentation of the spatial difference technique (left): one spectrum is recorded ON and another OFF the boundary. The amount of the dopant is estimated from the difference between the two spectra. The new CEP method (right) and results on Sb-rich and Sn-rich IBs in ZnO (below) [15,20,21].

The **concentric electron probe** (CEP) method is based on acquiring a sequence of EDS or EELS spectra with different beam diameters and the boundary always placed at the centre. Because the centre of analysis is identical for all measurements sample thickness variations have no influence on the accuracy of our measurements. The dependency between matrix ($I_M$) and dopant ($I_D$) intensity ratio $I_M/I_D$ vs. the beam diameter ($r$) can be described by a simple geometrical approximation [16,20,21]. One of the conditions that must be met if we want to obtain accurate results is that the dopant element is present only in the interface or has a very low solid solubility ($\chi$) in matrix phase. If the electron beam is wide and the solid solubility is high, then a considerable amount of the dopant signal stems from the bulk rather than from the boundary, and the resulting over-estimate of the effective boundary width can be very large. This effect would lead to a strong deviation from the linear dependence and to asymptotic convergence of the function $I_M/I_D=f(r)$ towards a constant value ($\chi$) for large beam sizes. In our case the dopant is present only in the IB plane. For very low solid solubility (lim $\chi \to 0$) the $I_M/I_D$ intensity
ratio is linearly dependent on $r$, where $I_M$ is proportional to the concentration of the matrix element in cylindrical volume (without the interface plane) excited by the incident electron beam of selected radius ($r$), whereas $I_D$ of the dopant element stems only from the interface [16]:

$$\frac{I_M \cdot c_D}{I_D \cdot c_M} = \frac{\pi}{2d} r - 1$$ (Eq. 2)

where $d$ is the arbitrary width of the interface occupied by the dopant element. To calculate the actual occupancy of the dopant, this value must be considered in terms of structural density for the specific crystallographic plane. IBs in ZnO lie in the basal planes of the wurtzite structure, which are separated at a spacing of $c/2=0.2605$ nm. In order to obtain the fraction of the interface occupied by the dopant element the arbitrary width $d$ must be divided by this value for ZnO.

Our HRTEM analysis [16] showed that Sb is perfectly ordered in the IB layer and occupies either 1/3 or 2/3 of the IB octahedral sites. The results of our quantitative CEP/EDS analysis of three different IBs showed that Sb occupies 0.326 ± 0.040 of the IB-layer, which is close to 1/3 of a monolayer. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) studies of Sb-rich IBs confirmed the observed occupancy and a hexagonal ordering of Sb and Zn atoms in the IB plane [23]. Using complementary imaging and analytical techniques we could estimate the actual accuracy and precision of CEP method and quantitatively compare it with the spatial difference technique. In analytical methods only precision (statistical error) can be estimated, but the most important parameter accuracy is never discussed because of the lack of independent measurements or theory that would provide a reliable estimate of the measured quantity. Based on complementary structural studies [16] we know that in the case of Sb-rich IBs antimony occupies 1/3 of the boundary monolayer (highly ordered hexagonal arrangement). Hence the actual accuracy and precision of both methods can be estimated. The accuracy of the spatial difference measurement [13] was poor ±300%, whereas the accuracy of CEP measurements [16] approaches ±2%, which is two orders of magnitude better than any other analytical method! Most of the improvement is due to elimination of systematic errors by the CEP method. Precision, on the other hand, can be improved by careful experimental work and was ±50% for spatial difference measurement [13] and ±12% for the CEP method. More detailed theoretical background and the capabilities of the CEP method are given elsewhere [20-22]. The atomic fractions of Sn-rich and Fe-rich IBs in ZnO showed occupancies of 0.504 ± 0.038 [20-22] and 1.018 ± 0.076 [21], respectively. Both analytical methods are schematically illustrated in Figure 5.

4.3. Atomic arrangement in the IB layer

The final questions related to the structure of IBs are related to crystal chemistry and local charge balance at the atomic scale. HRTEM studies and CEP measurements on IBs with different dopants indicated that the oxidation state of particular dopant dictates the atomic arrangement in the IB plane.

According to Pauling's electroneutrality principle for ionic crystals [24] every Zn$^{2+}$ in tetrahedral interstices of the ZnO structure obtains a charge of $\frac{1}{2} e^-$ from each of the four closest O$^{2-}$ ions and the average charge per tetrahedral site in the wurtzite structure is +II. Every cation located in the IB octahedral interstice, however, has six neighbouring O$^2-$, which produces an average charge per octahedral site of +III [16]. To satisfy the local charge balance according to Pauling's rule the expected in-plane composition of Sb-rich IBs would be SbZn$_2$, where one Sb$^{5+}$ alternated with two Zn$^{2+}$ cations would result in requested average oxidation state of +III for octahedrally coordinated cation in the IB plane. This is consistent with quantitative structural and chemical analysis of Sb-rich IBs [16].
Figure 6. Atomic model of Sb-rich IBs in ZnO reconstructed from (a) [2110] and (b) [0110] projections of the interface. In [2110] view the atomic columns in the IB plane have equal intensity, which implies that their composition is identical. In [0110] view, however, an interesting in-plane periodicity is revealed, suggesting that the atomic columns have two different atomic densities. Based on these contrast features, CEP analysis of IBs and Pauling’s principle of electroneutrality in ionic crystals the actual IB composition can be resolved [15].

Figure 6 shows HRTEM images of Sb-rich IB in ZnO in two low-index crystallographic orientations where the IB plane is viewed edge-on. From these two projections an atomic arrangement of the IB plane was reconstructed. Sb and Zn atoms in the IB plane form a highly ordered octahedral layer with a three-fold in-plane symmetry in the ratio of Sb:Zn=1:2 [16]. In this analogy we predicted that IB-layers with other pentavalent dopants (M⁵⁺) should have similar atomic arrangement with an IB-layer composition of MZn₂ (1:2), tetravalent dopants (M⁴⁺) will have an IB-layer composition of MZn (1:1), and trivalent dopants (M³⁺) would form a full IB-layer M (1:0) of the corresponding dopant element. Investigations of Sn(IV)-rich and Fe(III)-rich IBs in ZnO have supported this prediction [21].
5. Nucleation and growth of inversion boundaries

Top-down structural analysis of IBs has clearly indicated that the main driving force for the inversion is the preservation of the local charge balance upon incorporation of IB-forming dopants. In the next step we have designed experiments to study the nucleation and growth of IBs in different systems. Experiments using ZnO single crystals embedded into ZnO powder with the addition of SnO$_2$, Sb$_2$O$_3$ and In$_2$O$_3$ [19] showed that, depending on the oxidation state of the dopants, we can identify two competing mechanisms of IB nucleation: (i) internal diffusion, and (ii) surface reaction and growth. The first mechanism is characteristic for +III dopants and is controlled by Zn-vacancy diffusion mechanism, whereas the second mechanism holds for all IB-forming dopants and is controlled by chemisorption of the dopants on Zn-deficient (0001) surfaces. Grain growth studies of ZnO ceramics have indicated that IBs are growth faults that control the growth of ZnO grains. Grain growth experiments showed that IBs form prior to the spinel phase in a particular phase system and grains with IBs grow exaggeratedly at the expense of normal ZnO grains until they dominate the microstructure [8].

5.1. Internal diffusion and surface reaction mechanisms of IB formation

To resolve the mechanism of IB formation we have to understand the principles of dopant diffusion into the ZnO structure and thermodynamics of chemical reactions that take place on the surface of growing ZnO grains. The diffusion of isovalent dopants into the ZnO structure can be explained by zinc self-diffusion and its evaporation at higher temperatures [25]. Evaporation of Zn atoms from the (0001)-Zn surfaces produces clusters of Zn-vacancies, which are more stable than isolated vacancies [29]. The easiest path for diffusion of Zn-vacancies and vacancy clusters are the close-packed (0001)-Zn planes, while Zn$^{2+}$ ions were predicted to move more rapidly by jumping through a series of octahedral sites lined along the close-packed Zn-layers. At elevated temperatures the mobility and evaporation of Zn atoms near the surface of ZnO crystals becomes significant and the near-surface concentration of Zn-vacancies is increased. The cation diffusion mechanism would apply for any +II dopant that forms a solid solution with ZnO without changing the basic ionic configuration of the wurtzite structure [25]. Local charge deficiency, caused by the formation of Zn vacancies at elevated temperatures, is therefore compensated for by the incorporation of the dopant elements.

Zn deficiency may also be the main driving force for the migration of +III ions into close-packed basal planes of ZnO. On their path the +III ions would preferentially occupy the larger octahedral sites rather than the tetrahedral sites. In order to reduce the induced surplus of charge Zn$^{2+}$ ions from the adjacent wurtzite layer are shifted from the type-I to the type-II tetrahedral sites, producing the head-to-head inversion boundary [16]. This generates a charge deficiency in the next Zn layer and triggers a progressive relaxation (inversion) of the complete ZnO domain. The charge balance of the entire ZnO crystal is achieved when the charge-relaxation front exits the crystal. Following the cation diffusion mechanism, accompanied by an inversion of the adjacent ZnO domain, the +III ions may propagate along parallel basal planes deep into the ZnO crystal, producing multiple parallel IBs on their way. Such cases are known in ZnO-Fe$_2$O$_3$ [26,27], ZnO-Ga$_2$O$_3$ [28] and ZnO-In$_2$O$_3$ [19,27] systems.
Figure 7. Initial stages of IB nucleation at 780°C in the ZnO-SnO$_2$ system (left). The temperature of IB formation is lower than the spinel-phase formation temperature. The illustration (on right) shows the basic principle of IB nucleation following the surface reaction mechanism that applies for +IV and +V dopants. To maintain the local charge balance the adjacent ZnO domain grows in inverted orientation with respect to the IB plane.

The dopants that have a higher oxidation state than +III follow a different nucleation mechanism because the surplus of charge brought by these dopants cannot be simply compensated by the internal diffusion. Instead these dopants use the weakness of Zn-vacancy clusters on the (0001)-Zn surfaces [29]. The octahedral sites located at the centres of these vacancy clusters would be very favourable for chemisorption of the IB-forming dopants. This process leads to formation of a stable (two-dimensional) surface compound. To avoid unfavourable face-sharing with neighbouring tetrahedral sites Zn$^{2+}$ ions jump to their closest octahedral interstices, forming a mixed octahedral layer together with the IB-forming dopant. As soon as the octahedral interstices are occupied, the wurtzite structure on top of the IB layer starts to crystallise in an inverted orientation with respect to the base crystal, as illustrated in Figure 7. The main reasons for crystallisation in the inverted orientation are preserving the local charge balance, avoiding octahedral-tetrahedral face-sharing, and minimising the short-range cation-cation repulsion forces. To satisfy the local charge balance, the dopant ions are ordered in the IB layer in an appropriate ratio with the Zn$^{2+}$ ions to satisfy the average oxidation state per IB in a terstitial site of +III that fulfils the charge balance for head-to-head IBs in ZnO [16].

5.2. Stability of the IB-layer and its influence on ZnO grain growth

Let us take a look on the thermodynamic reasons for IB nucleation. The necessity of the presence of IB-forming dopants to generate an IB implies that the resulting 2D structure embedded in the hosting crystal is more stable than the reactants alone (ZnO and the dopants). Nucleation of IB by either internal diffusion or surface nucleation causes local chemical reaction driven by the preservation of the local charge balance. The formation of such special boundaries, like IBs in ZnO, is therefore chemically triggered and takes place in the preparatory stage of binary-phase formation [30]. In general, the activation energy for the formation of special boundaries in host crystals is lower than the energy for the formation of the full binary phase. By low-temperature sintering of SnO$_2$-doped ZnO it was demonstrated that IBs nucleate below the formation temperature of the ZnSn$_2$O$_4$ spinel [19]. Because of the
intimate structural relationship with the host ZnO structure the crystals containing IBs compete for the same building material as the crystals without such defects. Grain-growth studies in various binary systems showed that the composite grains with special boundaries are more successful in growth than the normal grains, implying that the formation energy of composite grains is significantly lower than that of the host crystal alone. An initial stage of IB formation and nucleation mechanism by surface reaction and growth is illustrated in Figure 7.

After their nucleation, IBs grow via solid-state reaction taking place at the IB front. The formation of IB structure is an efficient way of lowering the system energy by incorporating the impurity atoms. In the initial stages of growth grains with IBs develop extremely anisotropic morphology. During their growth, islands of ZnO are topotaxially deposited on both sides of the IB-lamella. While the driving force for growth of such composite crystal with the direction of the inherent IB plane is the incorporation of the IB-forming dopant, the main reason for their thickening normal to the intrinsic IB layer in the second growth stage is the relatively large surface area of the (0001) terminations. In spite of the fact that the growth rate in [0001] direction is the slowest in ZnO [31], composite ZnO grains always have much larger curvature radii than normal ZnO grains, and they are always more successful in competition for building material (ZnO), regardless of the size of the normal grains [8]. The high stability of the composite grains and their ability to consume all the available ZnO has dramatic effects on microstructure development. Once an IB is formed this grain can never regress to a normal ZnO grain under regular conditions. The microstructures of fully evolved ZnO grains with IBs present a thermodynamically stable equilibrium state and typically show no further recrystallization [32].

5.3. Grain growth kinetics in ZnO ceramics in the presence of IBs

Time lapse grain growth experiments at different sintering temperatures revealed four distinct stages of microstructure evolution on doping with IB-forming additives were identified [32]: (i) nucleation of the IB on the surface of the primary ZnO grains, (ii) formation of composite ZnO( IB) grains followed by exaggerated anisotropic growth, (iii) thickening of the composite ZnO( IB) grains until all normal ZnO grains are consumed and (iv) reaching fully evolved equilibrium microstructure where all grains contain IBs. During nucleation the concentration of IBs is proportional to the amount of the added IB-forming dopant and the efficiency of the dopant distribution through the microstructure, i.e., Sb₂O₃ with a higher mobility produces a higher initial number of ZnO( IB) grains than the less mobile SnO₂ or TiO₂ at equivalent temperature and dopant concentration [33]. In the next stage many IBs that have formed on the surface of ZnO grains are dissolved, while some remain and start to grow anisotropically. The material needed for the growth of the ZnO( IB) grains is supplied from normal ZnO grains, which are dissolved in the growth process. The grain growth in this stage is entirely controlled by the IB-induced grain-growth mechanism until ZnO( IB) grains reach the mean free path between the ZnO( IB) nuclei. The mean free path for ZnO( IB) growth depends on the initial concentration of nuclei (Figure 8). The grain growth during this stage is very rapid and the apparent energy for the ZnO grain growth is the lowest during the entire growth process [32]. After impingement of the ZnO( IB) grains growth is controlled by the Ostwald's ripening mechanism, where the existing ZnO( IB) grains fill up the whole microstructure at the expense of the remaining normal ZnO grains. In this growth stage the grain-growth rate is slowed down while the apparent energy for ZnO growth is increased. Close to equilibrium only local recrystallization processes take place. During this final stage equilibrium grain boundaries are formed due to relative surface energies in particular crystallographic directions. During this stage the number of grains and their size does not change with sintering time [32].
6. Microstructural engineering of varistor ceramics

The knowledge about the atomic structure of IBs, local charge balance, the stability of the IB structure and the mechanisms of IB nucleation and growth can serve us to design experiments for optimization of the varistor’s physical properties. The main technological challenges would be to improve the electrical properties, design components for any desired voltage and reduce the production cost by lowering the amount of additives, shortening sintering time/temperature, etc. Can this be done?

In principle, we have demonstrated that lowering the amount of IB-forming dopant leads to the formation of coarse-grained microstructure. Such microstructure is desired in low-voltage applications. Sb₂O₃ is generally known as the dopant to produce fine-grained varistor ceramics, however, via the IB-induced grain growth mechanism it should be possible to obtain coarse-grained microstructures even with Sb₂O₃ if we start with fewer IB-nuclei. In our diffusion doping experiment we have shown that microstructure development in Sb₂O₃-doped ZnO is controlled entirely by the exaggerated growth of ZnO grains containing IBs, whereas the presence of spinel grains has absolutely no effect on the final grain size [32]. According to the proposed IB-induced grain growth mechanism grains with IBs (nuclei) grow anisotropically and exaggeratedly along the direction of the inherent IB plane and during growth they consume surrounding normal ZnO grains without IBs. The final grain size simply depends on the quantity of Sb₂O₃ addition. At higher Sb₂O₃ concentrations, more nuclei form in the beginning of the grain growth process, the growing grains collide sooner and the final grain size is smaller. On the contrary, lower Sb₂O₃ additions lead to larger grain size. Our calculations showed that the additions of <30 ppm of Sb₂O₃ would produce microstructures of ZnO grains larger than the grain size of undoped ZnO, while higher additions of Sb₂O₃ would lead to fine-grained microstructures [33].
These findings were implemented in optimization of ZnO-based varistor ceramics. First, addition of Sb$_2$O$_3$ was varied to study microstructure development in binary ZnO-Sb$_2$O$_3$ system [34]. It was found that additions of less than 75 (mol) ppm Sb$_2$O$_3$ lead to the formation of ZnO grains larger than that in the undoped ZnO ceramics. This value is about twice as high as the amount of Sb$_2$O$_3$ determined in the diffusion doping (in vapour phase) experiment [33]. Possible reasons for the loss of Sb are locally increased concentrations of Sb$_2$O$_3$ causing formation of nanosized Zn$_7$Sb$_2$O$_{12}$ spinel particles and evaporation of Sb$_2$O$_3$ at higher temperatures. After optimizing the processing parameters for the binary ZnO-Sb$_2$O$_3$ system other dopants were selectively added in order to produce the varistor effect (Bi$_2$O$_3$) and increase the conductivity of ZnO grains (Co$_2$O$_4$, Mn$_3$O$_4$, NiO, Cr$_2$O$_3$). With the addition of other dopants the total amount of Sb$_2$O$_3$ increases due to solid solubility of antimony in Bi-rich liquid phase and minor formation of Bi$_2$Zn$_2$Sb$_3$O$_{14}$ pyrochlore phase. To obtain the coarse grained microstructure up to 200 ppm of Sb$_2$O$_3$ are needed in complete varistor composition (Figure 9). Electrical measurements of this new generation of ZnO-based varistors show very promising nonlinearity coefficients ($\alpha \approx 40$) and low leakage current. Fundamental understanding of IB-induced grain growth in ZnO provided a solid foundation for completely new approach to tailor the microstructures of either low, medium or high-voltage varistor ceramics at radically lower amount of dopants, while gaining improved electrical properties at lower cost. Consequently varistor ceramics with the reduced amount of unwanted secondary phases at the GBs and increased effective contact area among the ZnO grains can be produced, providing improved energy absorption capability of varistors for any nominal voltage. Savings on raw material per varistor unit also give producers a considerable cost-advantage towards their competition at higher quality, and due to highly reduced concentration of heavy metal contaminants, also an ecologically advantageous product.
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