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Nucleation and growth of basal-plane inversion boundaries in ZnO

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Abstract

Grain growth studies of zinc oxide ceramics have indicated that inversion boundaries (IBs) are growth faults that control the growth of the zinc oxide (ZnO) grains. To substantiate this observation, we designed experiments to study the nucleation of IBs. Low-temperature experiments showed that in the ZnO–SnO_2 system, IBs form before the Zn_2SnO_4 spinel phase and grains with IBs grow exaggeratedly at the expense of the normal ZnO grains until they completely dominate the microstructure. Experiments using ZnO single crystals embedded into ZnO powder with the addition of SnO_2, Sb_2O_3 and In_2O_3 showed that depending on the oxidation state of the IB-forming dopant ions, there are two competing mechanisms of IB nucleation: (i) internal diffusion, and (ii) surface nucleation and growth. The first mechanism is typical for III+ dopants and is controlled by Zn-vacancy diffusion, whereas the second mechanism holds for all IB-forming dopants and is controlled by chemisorption of the dopants on Zn-deficient (0 0 0 1) surfaces. In both cases, the driving force for the inversion is the preservation of the local charge balance.

Keywords: Grain growth; Domain boundaries; ZnO; Varistors

1. Introduction

Zinc oxide (ZnO) based ceramics are commonly used in the production of a diverse range of electronic devices because of their semiconducting or even conducting properties. The most widespread use of ZnO is in the production of non-linear resistors, i.e., varistors.[1] The physical properties of varistor ceramics are modified by the addition of various dopants. One of the most important properties of a varistor which is closely related to the varistor's breakdown voltage, is the ZnO grain size. This grain size may be controlled by the addition of Sb_2O_3, TiO_2 or SnO_2.[2–4] All these dopants are known to form spinel phases with ZnO, and trigger the formation of inversion boundaries (IBs) in the ZnO grains. The addition of these dopants to ZnO results in the formation of a single IB per ZnO grain; however, the so-called III+ dopants, like In_2O_3, Fe_2O_3 or Ga_2O_3, induce the formation of many parallel IBs in the ZnO grains.[5–8]

In the early studies of ZnO grain growth, the spinel particle pinning mechanism was believed to be the major grain-growth controlling mechanism in ZnO ceramics;[2] IBs were not given much consideration. The actual role of IBs in ZnO grain growth was not identified until recently, when Daneu et al. demonstrated in SnO_2-doped ZnO that these planar defects play the major role in the growth of ZnO grains via the IB-induced grain-growth mechanism.[4] In addition, they proved that the spinel grains have no influence on the final ZnO grain size. The same principle has been confirmed in Sb_2O_3-doped and TiO_2-doped ZnO.[9,10]

For almost a decade, the IBs in ZnO served purely as a challenge to crystallographers, who studied their local structure. The first structural study of IBs in Sb_2O_3-doped ZnO was presented by Kim and Goo,[11] who anticipated that IBs are planar faults, free from any dopant. Further studies showed that in addition to Zn atoms, the composition plane of an IB incorporates Sb atoms,[12–15] which stabilise the IB structure and assist in the inversion of the ZnO crystal. The first experimental evidence that the presence of Sb is necessary for the stability of the IB structure was presented by Rečnik et al.,[14] who showed that when in a high-vacuum and heated by a high-energy electron beam, the IB disintegrates into a sphalerite stacking fault (SF) and an inversion twin, both of which are free of the dopant. However, in spite of understanding their structure and the necessity

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of certain dopants for the formation of IBs, better understanding of the way in which they facilitate the growth of ZnO grains along the IB plane is required.

In a recent growth-kinetics study using large ZnO crystals imbedded in ZnO powder, Lee et al.[16] demonstrated that the growth rate of a ZnO crystal is fastest in the $[0\,0\,0\,1]$ direction, this is followed by the growth rate of the hexagonal prismatic directions, and in the $[0\,0\,0\,\bar{1}]$ direction, the growth rate is the slowest. In the case of ZnO crystals that contain head-to-head IBs, the fast growing $[0\,0\,0\,1]$ directions of the two ZnO domains are oriented towards the IB composition plane, bringing the slowest growing $[0\,0\,0\,\bar{1}]$ direction to both the basal surfaces of such a crystal. This means that even without the special driving force of the boundary itself, such crystals would grow anisotropically parallel to the IB plane, while the growth rate normal to the $(0\,0\,0\,\bar{1})$ plane is expected to be low.[16] This study clearly shows that in pure ZnO, the head-to-head orientation of the ZnO domains would favour anisotropic growth along the IB plane; however, it does not explain why the grains with IBs grow faster than the normal ZnO grains.[4]

In order to link the structural properties of IBs and the orientation-dependent growth of ZnO crystals with the exaggerated growth of ZnO grains with IBs, we designed experiments to clarify the initial stages of the IB-formation, i.e. the nucleation of IBs. In the first part of our investigations, we studied the temperature of IB formation relative to the corresponding Zn-dopant spinel formation, and in the second part we investigated the early stages of IB nucleation using large ZnO single crystals imbedded and fired in ZnO powder doped with SnO_2, Sb_2O_3 and In_2O_3 additions.

2. Experimental

To examine the IB formation temperature relative to the spinel phase formation temperature we used the ZnO–SnO_2 system, in which the Zn_2SnO_4 spinel forms above 800 °C.[4] The specimen was prepared according to the standard ceramic procedure, by mixing oxide powders in ethanol. In our experiment we used a ZnO powder (Pharma A, Lot No. 031291303, average grain size $D \sim 0.6\ \mu m$) with the addition of 1 mol% of Bi_2O_3 and 0.1 mol% of SnO_2. The homogenised mixture was pressed into pellets and sintered at 780 °C for 16 h.

The IB nucleation was studied on commercially available single crystals of ZnO. The crystals with well-developed first-order prism faces were cut into 1-mm-thick slices normal to the *c*-axis. The slices, with a characteristic hexagonal cross-section, were mounted with one of their $\{1\,1\,\bar{2}\,0\}$ prism facets on a pre-sintered ZnO pellet, as illustrated in Fig. 1. To allow a uniform supply of spinel-forming dopants during the sintering the pellets with ZnO crystals were embedded in ZnO powders doped with 0.1 mol% SnO_2, Sb_2O_3 or In_2O_3. The powder beds were prepared according to the standard ceramic mixed-oxide procedure. The compacts were pressed isostatically and sintered for 16 h at 1200 °C.

The samples were examined using a scanning electron microscope (SEM; JSM-5800, JEOL, Tokyo, Japan) operated at 20 kV. For the SEM observations, the sintered compacts with the imbedded single crystals were cut parallel to the base ZnO pellet, as shown in Fig. 1. To expose the characteristic microstructural features and reveal the orientation of the *c*-axis of the individual ZnO domains,[4] the cross-sections of the specimens were polished and etched in dilute hydrochloric acid (H_2O:HCl = 20:1) for about 5 s.

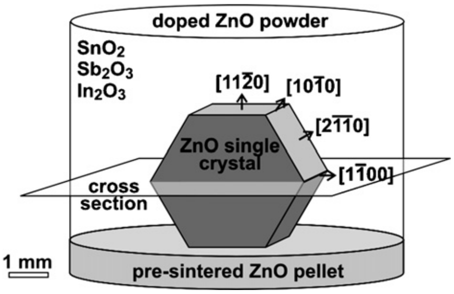

Fig. 1. Experimental set-up for sintering ZnO single crystals embedded in ZnO powder with the addition of three IB-forming dopants having different oxidation states: SnO_2, Sb_2O_3 and In_2O_3.

3. Results

3.1. Low-temperature sintering of SnO_2-doped ZnO powder

The microstructure of the ZnO specimen with the addition of 1 mol% Bi_2O_3 and 0.1 mol% SnO_2 sintered at 780 °C is shown in Fig. 2. The grain-growth kinetics at this temperature are slow, and therefore many ZnO grains remained small and kept their isometric shape. It is evident, however, that some ZnO grains grew significantly and that all these large grains contain an IB. The IBs are exposed after chemical etching because of the different orientation of the ZnO domains on both sides of the IB, and are visible as white lines intersecting some of the ZnO grains in all the SEM images. No $ZnSn_2O_4$ spinel grains were present in this specimen (checked in the unetched part of the specimen), which proves that in the ZnO–SnO_2 system the IBs form below the formation temperature of the Zn_2SnO_4 spinel phase. All the exaggeratedly grown grains are elongated in the direction of the IB, which is apparently their fastest growth direction. In most ZnO grains, the IBs intersect the grain through the middle; however, in some cases they appear to be located on the surface of the ZnO grain (Fig. 2b). There are even situations where only a small part of the IB is attached to the ZnO grain, while most of the IB stretches further into the polycrystalline ZnO matrix with a few pyramidal islands of ZnO here and there that crystallised on both sides of the IB. One such grain is marked in the lower middle part of Fig. 2a. It is also common for IBs to make steps to other basal planes of the ZnO crystal within a single ZnO grain (Fig. 2c). This may be explained by the multiple nucleation of IBs on different sides of the primary crystal. During further growth, the islands of oppositely oriented ZnO domains that nucleated at many points on the surface of the primary grain are finally merged.

From these observations, we can conclude that the IBs in the ZnO–SnO_2 system are special growth defects that nucleate epitaxially on the surface of the ZnO grains and, supported by

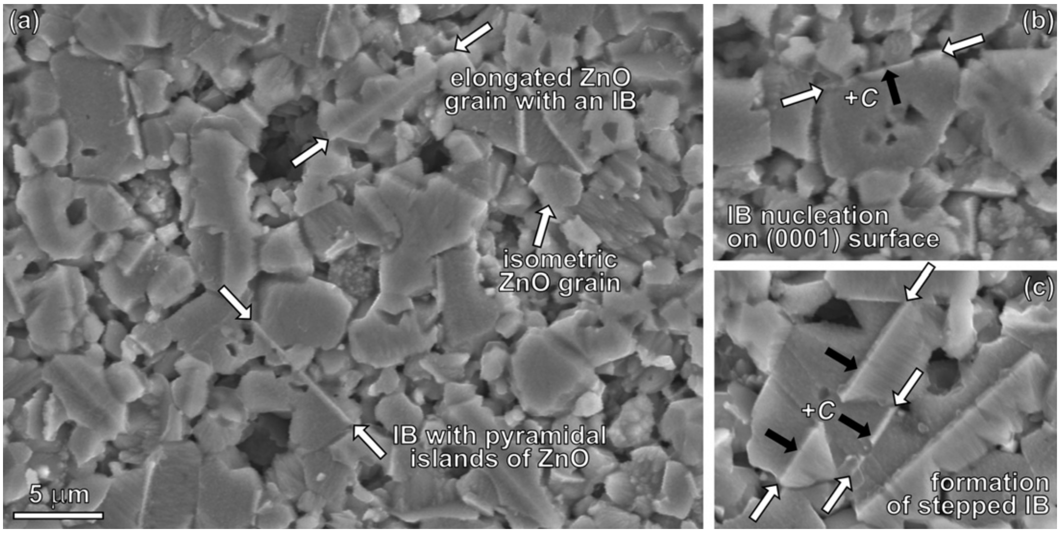

Fig. 2. (a) Etched microstructure of ZnO specimen with the addition of 1 mol% Bi_2O_3 and 0.1 mol% SnO_2 sintered at 780 °C for 16 h. IBs formed in many ZnO grains (indicated by arrows). (b) In the early stage, IBs often nucleate on the (0 0 0 1) surface of ZnO grains. The [0 0 0 1] direction of the polar *c*-axis is indicated by black arrows and is easily determined from the orientation of the triangular etch-pits. (c) ZnO grain with parallel IBs that nucleated at different locations on the surface of the grain, in effect a stepped IB is developed.

the ZnO crystal, they propagate along the fault plane as long as the following ambient conditions allow their formation: (i) a sufficient supply of the IB-forming dopant that stabilises their structure, (ii) the minimum temperature necessary for IB nucleation, and (iii) the free distance to the neighbouring grains with IBs.[4,9] The situation in Fig. 2a suggests that under certain conditions, the IB growth is considerably faster than the growth of normal ZnO grains. In the next part of our study, we investigated

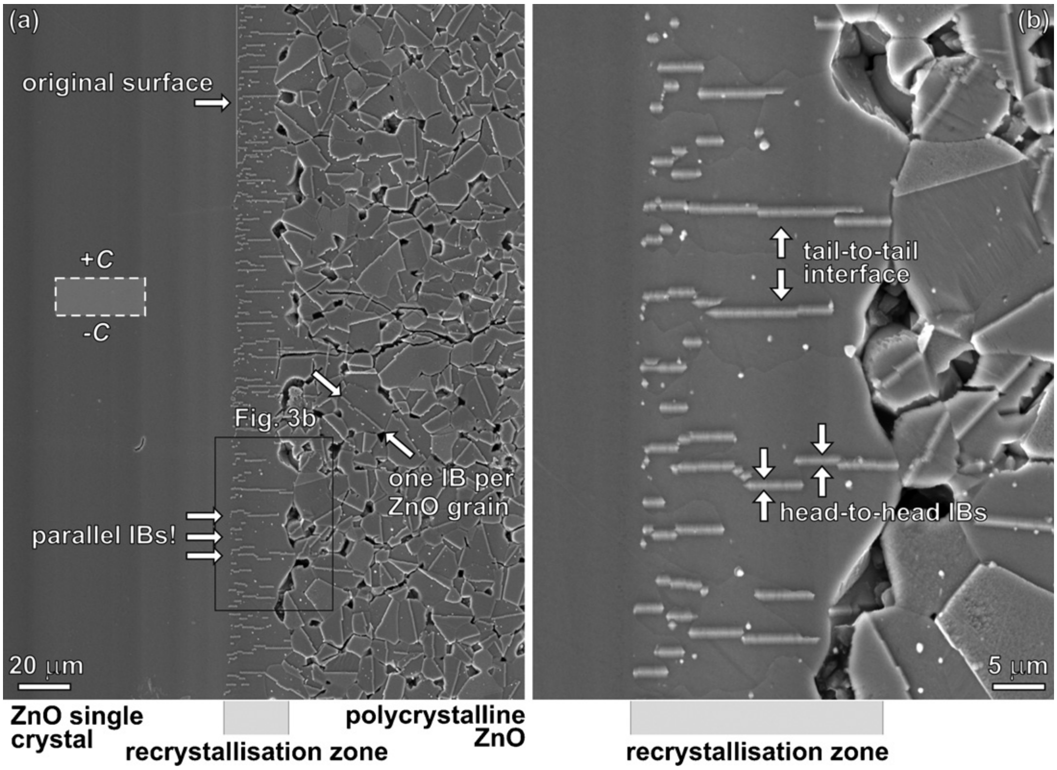

Fig. 3. (a) Recrystallisation on the prism surface of the ZnO single crystal after sintering in SnO_2-doped ZnO powder. No defects are observed in the interior of the single ZnO crystal; the recrystallisation zone starts at the surface of the crystal, where multiple parallel head-to-head IBs nucleated and grew into a polycrystalline ZnO matrix. (b) Close-up of the recrystallisation zone with parallel IBs. The impingement of the oppositely oriented ZnO domains results in the formation of secondary tail-to-tail interfaces (wavy boundaries with weak contrast between the primary head-to-head IBs).

the nucleation of IBs on single ZnO crystals in three different systems: ZnO–SnO_2, ZnO–Sb_2O_3 and ZnO–In_2O_3.

3.2. *Nucleation of IBs on a ZnO single crystal embedded in SnO_2-doped ZnO powder*

In our experimental set-up, the single crystal of ZnO may be considered as a single, very large grain in a matrix of many small ZnO grains. If we had normal recrystallisation conditions in this system, the large ZnO single crystal would eventually consume the small grains from the surrounding ZnO powder (the Ostwald ripening mechanism), however, due to the presence of the IB-forming dopant the normal grain-coarsening mechanism is overshadowed by the IB-induced exaggerated grain growth.[4,9–10]

On a cross-section of the SnO_2-doped ZnO single crystal, shown in Fig. 3a, we can see a 15–20-μm-thick recrystallisation zone on the $\{1 1 \bar{2} 0\}$ prism facets. We did not find any IBs on the basal surfaces of the crystal, and also in the interior of the crystal no changes were observed. The average ZnO grain size in the polycrystalline matrix around the single crystal is ∼20 μm. Every grain in the matrix contains a single IB, implying that the microstructure already reached its thermodynamically stable condition, where the ZnO grains with IBs consume all the normal ZnO grains,[4] which are used as a building material for their growth. The morphology of the IBs is either simple planar or stepped.

In the recrystallisation zone, the situation is more complex; it contains many parallel head-to-head IBs that nucleated on the prism facets of the single crystal. In the close-up (Fig. 3b), we can see that many IBs nucleated close to the surface of the single crystal, while relatively few of them actually survived and grew further into the polycrystalline matrix, forming a jagged interface. This suggests that there were many nucleation points for the formation of IBs on the surface of the single crystal, and during growth only a few IBs prevailed and continued their growth. This situation is somewhat similar to the formation of stepped IBs in polycrystalline ZnO, where IBs nucleate at different locations on the surface of the crystal and during growth they merge into a single stepped defect. It is because of the large surface of the embedded single crystal that so many IBs can coexist. They are separated by unfavourable pyramidal tail-to-tail interfaces, which are otherwise common in ZnO crystals doped with III+ IB-forming dopants like Fe_2O_3, In_2O_3 and Ga_2O_3.[5–8] These interfaces result from the impingement of the pyramidal ZnO islands that grow from the IB interface in the $[0 0 0 \bar{1}]$ direction. This can be compared to the formation of pyramidal islands on the single IB in the low-temperature sample, shown in Fig. 2a. The growth of the single crystal was stopped when the IBs in the recrystallisation zone collided with the grains with IBs that developed simultaneously in the surrounding polycrystalline ZnO. At this point, the microstructure reaches its energetically stable condition, and in contrast to the normal grain growth in undoped ZnO no further recrystallisation is possible.

3.3. *Nucleation of IBs on ZnO single crystals in Sb_2O_3- and In_2O_3-doped ZnO powder*

After sintering the ZnO single crystal in Sb_2O_3-doped ZnO powder, the prismatic surfaces show a lower degree of recrystallisation than in the SnO_2-doped sample. The recrystallisation zone is about 5 μm wide, which is comparable to the average grain size in the surrounding polycrystalline matrix. As shown in Fig. 4a, the domains with longer IBs extend further into the exterior. The main difference from the SnO_2-doped sample is that in the Sb_2O_3-doped sample the IB also formed on the $(0 0 0 1)$ surface of the single crystal. A segment of the $(0 0 0 1)$ surface of the single crystal with a thin inverted layer of ZnO is shown in Fig. 4b. The most straightforward proof of the polar *c*-axis direction is the orientation of the triangular etch-pits.[4] In Fig. 4b, the etch-pits in the single crystal are pointing toward the surface, showing that this facet is $(0 0 0 1)$ terminated, while the etch-pit in the thin recrystallised layer is pointing in the opposite direction, toward the white line in between, proving that this is in fact an $(0 0 0 1)|(0 0 0 1)$ IB. Below the $(0 0 0 1)$ surface, etch-pits are lined along the original surface of the single crystal. The recrystallised layer is ∼1.7 μm wide, which is about three times less than the width of the recrystallisation zone on the prism surfaces. As expected from their crystallography,[14] no IBs were found on the opposite $(0 0 0 \bar{1})$-O surface of the single crystal.

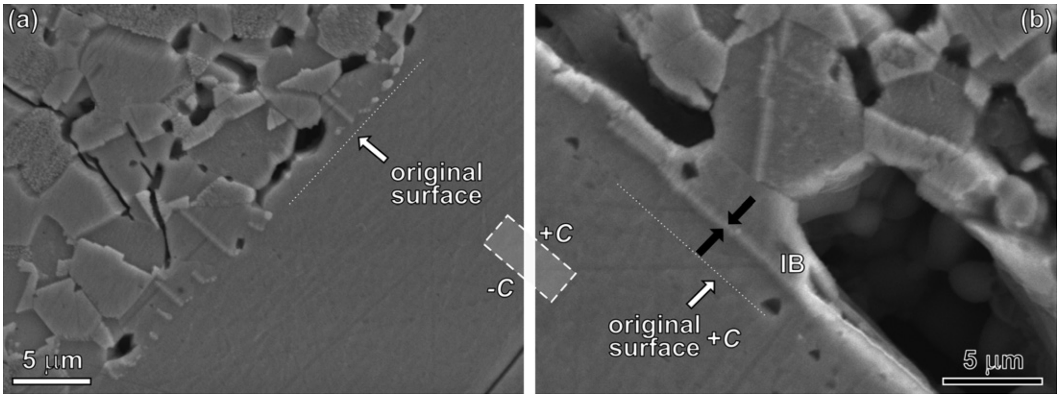

Fig. 4. (a) Recrystallisation on the prism surface of the ZnO crystal in Sb_2O_3-doped ZnO is significantly lower than that in the SnO_2-doped sample. (b) The formation of a head-to-head IB on the $(0 0 0 1)$ surface of the single crystal.

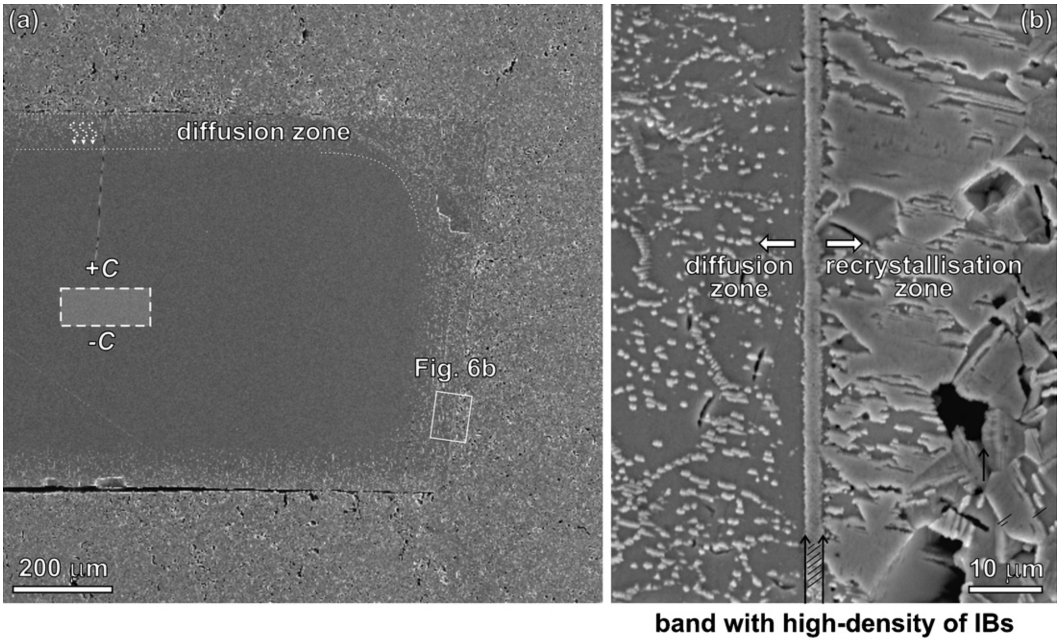

Fig. 5. (a) A wide diffusion zone with many defects indicates intense bulk diffusion of indium into the single crystal. (b) In the diffusion zone (left) many basal-plane IBs are formed, while on the surface we observe a thick recrystallisation zone (right), densely populated with IBs. The density of IBs is the highest near the original prism surface of the ZnO single crystal.

The effect of In_2O_3 doping on the recrystallisation of the ZnO single crystal differs significantly from the previously studied systems with SnO_2 and Sb_2O_3 additions. In addition to a surface recrystallisation, the indium diffused rapidly into the ZnO crystal and formed a 100-μm-wide diffusion zone full of small IBs formed in the interior of the crystal (Fig. 5a). The outline of the diffusion zone suggests the homogeneous diffusion of indium from all surfaces of the single crystal. An enlarged image of the recrystallisation zone on the prismatic surface, shown in Fig. 5b, reveals that at the original surface of the single crystal a 2-μm-wide band with a high density of IBs was formed. On the top of this band an approximately 20-μm-wide recrystallisation zone formed, similar to those in the SnO_2 and Sb_2O_3 systems. The large domains that formed on the prism surfaces of the crystal closely resemble the microstructure of individual ZnO grains in the polycrystalline matrix, where each grain contains several IBs separated by pyramidal faults. The presence of both diffusion and recrystallisation zones in this sample suggests that two competing mechanisms of IB nucleation are present in In_2O_3-doped ZnO.

4. Discussion

The results of our experiments have shown that during the sintering of ZnO single crystals embedded into SnO_2- and Sb_2O_3-doped ZnO powder the IBs formed only in the recrystallisation zone on the surface of the single ZnO crystal, while no IBs were observed in the interior of the single crystals. This indicates that the basal-plane IBs in these two systems form by surface nucleation and growth, and are not produced by the internal diffusion of the dopant. On the other hand, in the In_2O_3-doped ZnO sample the IBs are abundant in the interior as well as on the surface of the imbedded single crystal. In the following, we explain the two competing mechanisms of IB nucleation in ZnO.

4.1. *Nucleation of IBs by an internal diffusion mechanism*

ZnO doped with IB-forming dopants that have an oxidation state of III+,[5–8] or AlN doped with oxygen[18] are known to produce multiple IBs in the host crystal; however, the previous studies provided no in-depth information about the diffusion-controlled nucleation of IBs that could explain the presence of IBs in the interior of our In_2O_3-doped ZnO single crystal.

The mechanism of dopant diffusion into the ZnO structure can be explained by zinc self-diffusion and evaporation at higher temperatures. Tomlins et al.[19] reported that Zn diffusion is controlled by a Zn-vacancy (V_{Zn}) mechanism, and the recent scanning tunnelling microscopy (STM) study by Dulub and co-workers[21] showed that the evaporation of Zn atoms from the (0 0 0 1)-Zn surfaces produces triangular clusters of Zn-vacancies, which are more stable than isolated Zn-vacancies.[22] The easiest paths for the diffusion of Zn-vacancies and vacancy clusters are the close-packed (0 0 0 1)-Zn planes, while Zn^{2+} ions were predicted to move more rapidly by jumping through a series of empty 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. The local charge deficiency, caused by the formation of Zn vacancies at higher temperatures, is compensated for by the incorporation of dopant elements. The Zn deficiency may also be the driving force

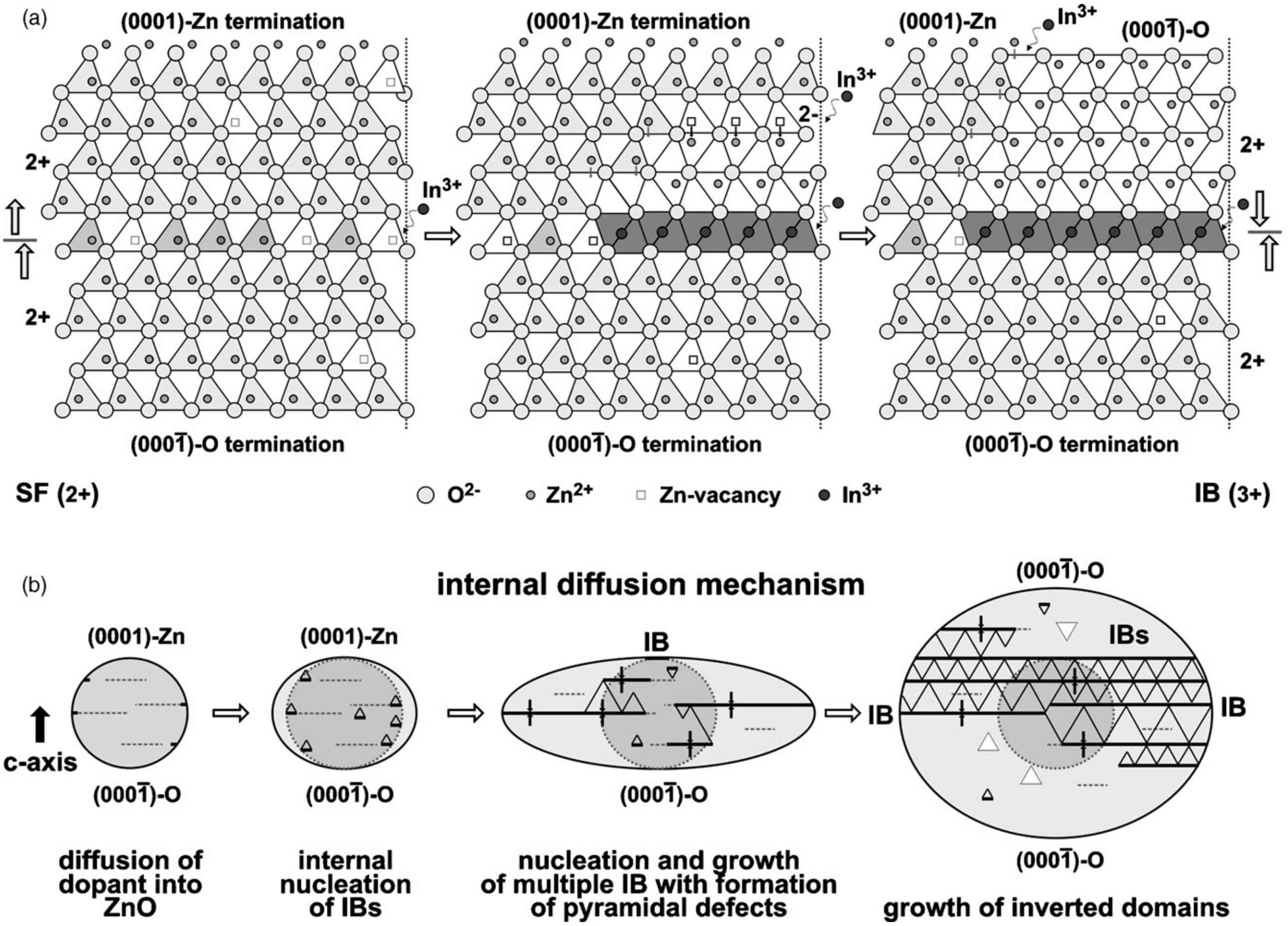

Fig. 6. (a) A schematic representation of IB nucleation by the internal diffusion mechanism. Local charge deficiency (Zn-vacancies) triggers incorporation of dopant ions (In^{3+}). The sites prone to the IB nucleation (structure!) are SFs (grey tetrahedrons). Dopant ions occupy the octahedral interstices, while the charge surplus is compensated for by the inversion of the adjacent ZnO domain (light-grey tetrahedrons). The inversion front (tail-to-tail) is constantly charge deficient and is a likely path for the further migration of dopant ions to the nucleation sites. (b) Early stages of ZnO grain growth with III+ IB-forming dopants. In the first step, IBs are formed at many sites near the surface of the ZnO grain. This is followed by the propagation of IBs into the initial grain (diffusion), as well as by their surface nucleation and growth (recrystallisation). Multiple IBs with intermediate pyramidal faults are basic characteristics of ZnO grains with III+ dopants.

for the migration of III+ ions into the close-packed basal Zn-V_{Zn} planes of ZnO. On their path the III+ ions would preferentially occupy the six-fold coordination sites rather than the regular tetrahedral Zn^{2+} sites. In order to reduce the induced surplus of charge in this layer, the Zn^{2+} ions from the adjacent wurtzite layer are shifted from the type-I to the type-II tetrahedral sites, i.e., the head-to-head orientation.[14] This generates a charge deficiency in the next Zn layer and triggers a progressive relaxation (inversion) of the whole 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 facing ZnO domain, the III+ ions propagate along the basal Zn-V_{Zn} planes deep into the ZnO crystal. The inversion front propagating in the $(0\,0\,0\,\bar{1})$ direction (normal to the IB-plane) is constantly charge deficient and as such is a favourable path for the migration of dopants to the IB plane (Fig. 6a). This would explain the wide diffusion zone rich in IB domains in the In_2O_3-doped sample. The highest concentration of IBs is near the surface of a single crystal, where the concentration of V_{Zn} is expected to be high. In contrast, deeper in the crystal, their concentration is depleted, which also indicates a diffusion-controlled process for their formation. Ions located at the IB form a close-packed octahedral layer with an average oxidation state of III+, consistent with the crystal chemistry study of wurtzite structures by Gehman and Austerman[22] and the IB structure analysis by Rečnik et al.[14] The internal diffusion mechanism for the formation of IBs is illustrated in Fig. 6a.

In ZnO, only the III+ dopants, such as In^{3+}, Fe^{3+} and Ga^{3+},[5–8] form IBs via the described internal diffusion mechanism, for the IV+ (Sn^{4+}) and V+ (Sb^{5+}) dopants this mechanism was not confirmed (this study). A common feature of these systems is the formation multiple IBs, such as those observed in the recrystallisation zone and in the ZnO grains of the In_2O_3-doped sample. The reason for the formation of multiple IBs is the simultaneous diffusion of the IB-forming dopant along several basal planes. The most likely sites for the nucleation of IBs are the existing basal-plane SFs that are very common in ZnO. Between two head-to-head IBs, the formation of a secondary interface with a tail-to-tail configuration is inevitable. In contrast to AlN,[18] this

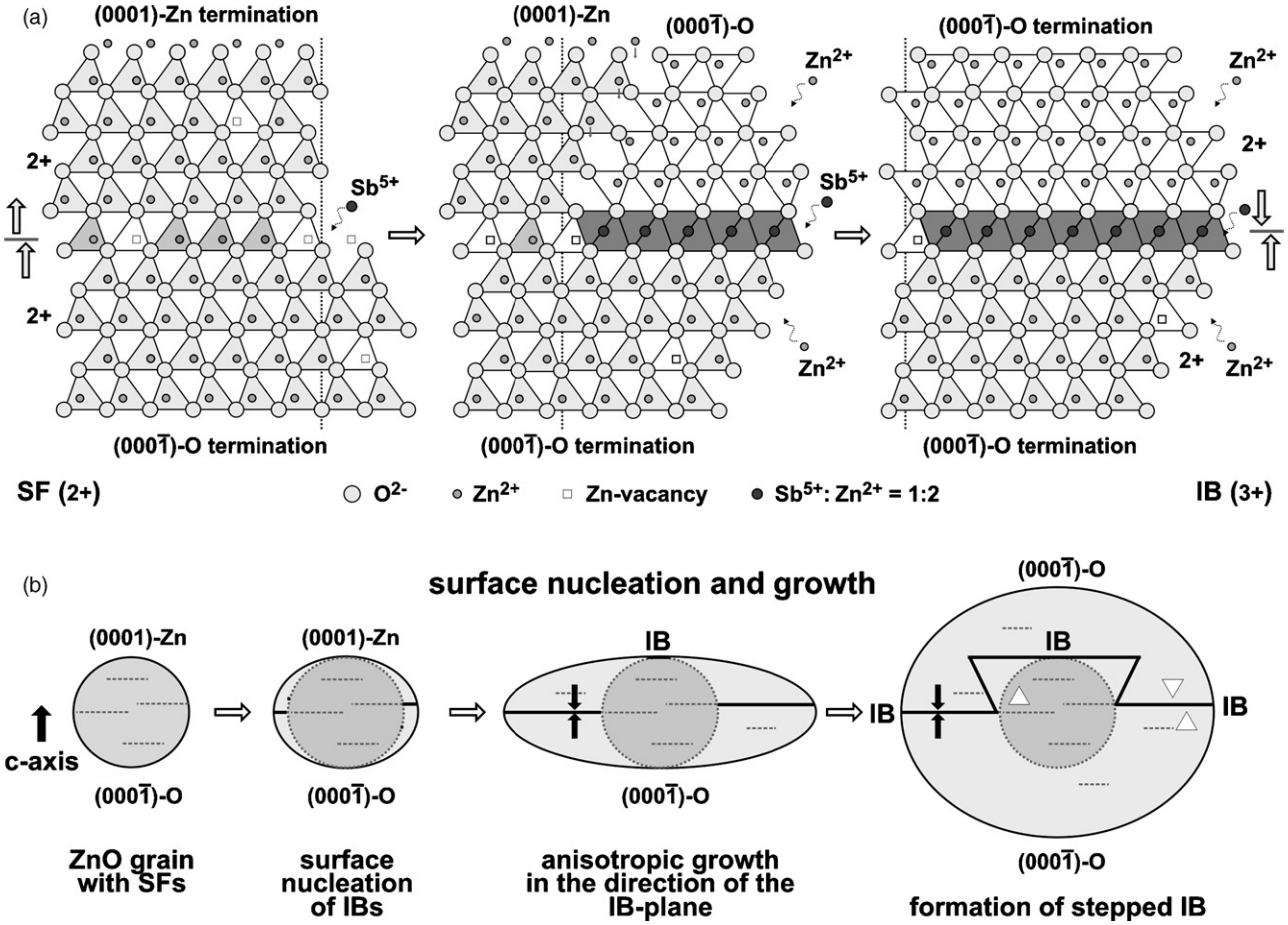

Fig. 7. (a) A schematic representation of IB nucleation by the surface nucleation and growth mechanism. Nucleation of IBs is controlled by the chemisorption of dopant ions to the available octahedral sites (triangular Zn-vacancy clusters) on exposed (0 0 0 1)-Zn surfaces of the ZnO crystal. Dopants are ordered with zinc to build a mixed IB-layer with an average oxidation state per octahedral site of III+. After nucleation, the IB-layer grows along the basal IB-plane, and the cladding ZnO domains follow its direction by crystallisation in the inverted orientation. (b) In the early stages of IB formation, many IBs form on the surface of the initial crystallite. Followed by growth, only one IB prevails. Multiple surface nucleation of IBs leads to the formation of stepped IBs. In the first stage of sintering, grains with IBs grow extremely anisotropically in the direction of the IB-plane, while in the late stages of sintering these grains thicken until they consume all normal ZnO grains.

configuration is highly unfavourable in ZnO, which leads to the formation of equilibrium pyramidal interfaces between the basal IBs. In In_2O_3-doped ZnO, the pyramidal domains produce semi-hexagonal chain-like patterns in the (0 0 0 1) planes, as shown by Loewe.[5] In view of the experimental observations, it is not clear why IBs do not form by internal diffusion with dopants that have a higher oxidation state than III+. One possible reason is that the surplus of charge brought by these dopants cannot be easily compensated for by this mechanism.

4.2. Surface IB nucleation and growth mechanism

In all three samples with SnO_2, Sb_2O_3 and In_2O_3 additions, IBs formed on the surfaces of the ZnO single crystals. The highest concentration of IBs was observed in the recrystallisation zone on the prism faces, while the basal surfaces showed very limited recrystallisation, and only in the Sb_2O_3-doped sample did a single IB form on the (0 0 0 1)-Zn surface. The reason for the formation of only one IB is crystallographic: once an IB is formed on the basal surface it develops a (0 0 0 $\bar{1}$)-O termination and permanently prevents the nucleation of another IB.

The crystallographic conditions for the formation of IBs are incomparably more favourable on the prism surfaces of the single crystal. Here, the IBs may form in abundance without obstructing each other in the nucleation stage. The most probable sites for the nucleation of IBs on the prismatic surfaces are the atomic steps, where the (0 0 0 1) planes are locally exposed and the dopant ions can be deposited. According to Rečnik et al.,[14] IBs involve two crystallographic operations: a basal-plane SF and an inversion of the upper domain, suggesting that SFs would be the most favourable locations for the nucleation of IBs. SFs represent planar errors in the wurtzite stacking and they either terminate with partial dislocations at any point within the crystal, or extend to the surface of the ZnO crystal. On the SF layer, the IB-forming dopant ions occupy the six-fold coordination interstices, i.e., octahedral for Sb^{5+}.[14]

According to the model of triangular Zn-vacancy clustering on the (0 0 0 1)-Zn surfaces,[20,21] the octahedral sites located at the centres of the vacancy clusters would be very favourable for the chemisorption of the IB-forming dopants. This process may be regarded as the formation of a sort of stable two-dimensional, surface compound. To avoid face-sharing with neighbouring tetrahedral sites the Zn^{2+} ions jump to their closest octahedral interstices, forming a mixed octahedral layer together with the IB-forming dopant. As soon as the six-fold 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 shown in Fig. 7a. The reasons for crystallisation in the inverted orientation are preserving of 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 the proper ratio with Zn^{2+} ions. In Sb_2O_3-doped ZnO, the ratio of Zn^{2+}:Sb^{5+} = 2:1,[14] whereas in the SnO_2-doped ZnO, the ratio of Zn^{2+}:Sn^{4+} = 1:1,[15] satisfying the average oxidation state per IB interstitial site of III+ that fulfils a charge balance for head-to-head IBs in ZnO.[14,22] In a structural study of IBs in Sb_2O_3-doped ZnO, Rečnik et al.[14] proved that the evaporation of antimony from an IB in a thin crystal foil under high vacuum causes its disintegration into a SF and a pyramidal inversion, suggesting that IB-forming dopants are necessary to stabilise the IB structure.

Our single-crystal experiments give us a valuable insight into the nucleation stage of IB formation. In the recrystallisation zone of the SnO_2- and Sb_2O_3-doped samples, many parallel head-to-head IBs nucleated at the surface of the single crystal, while only a few actually survived and grew to the surface of the zone. The reasons for the extinction of some IBs could be the higher growth rate of the larger IBs and the lack of dopant nourishing their growth. Between the IBs, secondary tail-to-tail boundaries formed as a result of the oppositely growing ZnO domains impinging. These interfaces occasionally adopt pyramidal planes, similar to the stepped defects in polycrystalline SnO_2- and Sb_2O_3-doped ZnO. Just like the large single crystal, the surfaces of smaller ZnO grains may also have several sites available for the nucleation of IBs. Namely, if two IBs nucleate independently on the opposite prism sides of the ZnO grain, the inverted domains developed on the top of the IB layers eventually overgrow the primary ZnO grain forming a stepped pyramidal boundary, and another head-to-head IB on the top (0 0 0 1) surface of the initial ZnO grain. The formation of stepped IBs that regularly appear in ZnO ceramics can therefore be explained by a multiple IB nucleation on the surface of the ZnO grains, as shown in Fig. 7b.

The nucleation of IBs with IV+ or V+ dopants is basically similar to that of III+ dopants. The only distinction is that III+ dopants propagate along the basal planes into the crystal, and on their path the upper ZnO domain is inverted, while in the case of IV+ and V+ dopants the IB layer nucleates on the surface of the crystal and the adjacent ZnO domain grows in an already-inverted orientation on the top of the IB-layer. In both cases, the main driving force for the inversion is the preservation of the local charge balance. It is important to note that the surface nucleation and growth mechanism was also confirmed in the In_2O_3-doped sample, which suggests that with the III+ dopants we have two competing mechanisms of IB formation in ZnO (Fig. 6b).

4.3. The role of IBs in grain growth and microstructure development of ZnO ceramics

Even more interesting are the thermodynamic reasons for IB nucleation. The necessity of the presence of IB-forming dopants to generate IBs implies that the resulting IB structure is thermodynamically more stable than the reactants alone (ZnO and the dopants). The formation of special boundaries, such as IBs in ZnO, is chemically triggered and can be related to the preparatory stage of binary-phase formation.[17] In general, the activation energy for the formation of such special boundaries in the host crystal seems to be much lower than the energy for the formation of the binary phase. In our low-temperature sintering of SnO_2-doped ZnO, we have shown that IBs form below the formation temperature of the $ZnSn_2O_4$ spinel, supporting the above suggestion. Because of their intimate structural relationship with the host structure the crystals containing special boundaries compete for the same building material as the bulk crystals with no such defects. Grain-growth studies in various binary systems,[17] including ZnO,[4,9,10] showed that the composite grains containing special boundaries are more successful at growth than the normal grains, implying that their formation energy is significantly lower than that of the host crystal alone.

After their nucleation, IBs rapidly grow in the direction of the IB layer as long as the supply of the ions necessary for their crystallisation is available. As shown by the low-temperature sintering of SnO_2-doped ZnO, in the initial stages of their growth IBs develop an extremely anisotropic morphology, and during the growth, islands of ZnO are deposited on both sides of the IB lamella. While the driving force for their growth in the direction of the IB plane is the incorporation of the IB-forming dopant, the main reason for their thickening in the direction normal to the intrinsic IB layer is the relatively large surface area of the $(0\,0\,0\,\bar{1})$ terminations. In spite of the fact that the $[0\,0\,0\,\bar{1}]$ direction has the slowest growth rate of all the directions in ZnO,[16] the curvature radius of these surfaces is incomparably larger than that of normal ZnO grains, and therefore grains with IBs are always more successful when competing for the building material, regardless of the size of the normal grains. And what is more, all normal ZnO grains are used up for their growth.

The high stability of ZnO grains with IBs and their ability to consume the available ZnO for their growth has dramatic effects on the microstructure development. Once an IB is formed within a ZnO grain, this grain cannot change back into a normal ZnO grain under regular sintering conditions. They can only grow and thicken as long as the normal ZnO grains are available. In SnO_2-doped ZnO, Daneu et al.[4] showed that in the early stages of sintering, normal ZnO grains and the grains with IBs coexist for a very short time; until the grains with the IBs consume all the normal ZnO grains and finally prevail. Based on these observations the authors developed the concept of IB-induced grain growth,[9] correlating the initial concentration of IB-forming dopant with the number of IB nuclei and the final grain size in Sb_2O_3-doped ZnO ceramics. Our single-crystal experiments showed that ZnO grains with IBs grow preferentially, even when competing with very large ZnO single crystals. Due to a homogeneous distribution of the dopant the IBs did not develop only on the surfaces of the single crystal, but also in the surrounding ZnO grains. ZnO grains in the matrix, and in the recrystallisation zone of the single crystal, grew only to the point when all the normal ZnO grains were consumed. After this stage, the microstructure shows no further recrystallisation regardless of the presence of a large single crystal. The average grain sizes are consistent with the grain sizes reported for such amounts of dopants in ZnO.[4,9] If we take into consideration the growth rates in different directions in undoped ZnO, recently reported by Lee et al.,[16] and the measured widths of the recrystallisation in our samples (the basal and prism directions), we can see that the growth rate normal to the prism planes is due to the rapid growth of IBs about 10 times faster than that in the undoped ZnO. Without the IB-forming dopant, the thermodynamically unstable state of the ZnO single crystal embedded in an environment of 1000 times smaller grains would reach equilibrium when the crystal overgrows the surrounding ZnO grains; however, in the presence of these dopants the ZnO grain growth is entirely controlled by the growth of the IBs. The microstructures composed of ZnO grains with IBs are thermodynamically stable, and typically show no further recrystallisation.

5. Conclusions

The nucleation of IBs in ZnO takes place at temperatures lower than the formation temperature of the binary phase that exists between ZnO and the IB-forming dopant (usually a spinel phase). Once an IB is formed in the ZnO grain, this grain cannot recrystallise back into a normal ZnO grain. ZnO grains with IBs consume all the normal ZnO grains until they prevail in the microstructure.

We have demonstrated that the nucleation of basal-plane head-to-head IBs in ZnO depends on the oxidation state of the IB-forming dopant ions. Two competing mechanisms of IB nucleation were identified for ZnO single crystals fired with SnO_2, Sb_2O_3 and In_2O_3 additions:

(1) Internal diffusion mechanism: controlled by a Zn-vacancy diffusion in the close-packed (0 0 0 1)-Zn planes. Dopant ions with a higher oxidation state occupy the octahedral interstices and the ZnO domain is inverted to preserve the local charge balance at the IB layer. This mechanism operates with dopants that have an oxidation state of III+ (e.g., In^{3+}).

(2) Surface nucleation and growth mechanism: controlled by the chemisorption of the dopant ions to the available octahedral sites in Zn-vacancy clusters on the (0 0 0 1)-Zn surfaces, where they form an octahedral composition plane together with Zn^{2+} ions that have an average oxidation state of III+. To preserve the local charge balance the ZnO domain grown on the top of the IB layer crystallises in the inverted orientation. This mechanism is specific for the IV+ (Sn^{4+}) and V+ (Sb^{5+}) dopants, and was also confirmed for the III+ dopants.

After nucleation, the IBs grow via a solid-state reaction taking place at the IB front. The formation of an IB structure is an efficient way of lowering the system energy by incorporating impurity atoms. A common feature of the initial stage of IB formation is the multiple nucleation of IBs. In systems where the nucleation of IBs is controlled by the internal diffusion mechanism, multiple parallel IBs are stable (III+ dopants), while in systems where the formation of IBs is controlled by surface nucleation and growth only one IB prevails in the crystal (IV+ and V+ dopants).

In addition to their controlling role in microstructure development, grains with IBs have a significant effect on the electrical properties of ZnO ceramics simply because of head-to-head inversion, which causes doubling of the $(0\,0\,0\,\bar{1})$-O terminating surfaces on the ZnO grains.[14,23]

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