Structural multiplicity in Pr-doped ZnO [0001] 27.8° and 30.0° Tilt Grain Boundaries

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Introduction

Zinc oxide (ZnO) ceramics doped with praseodymium (Pr) exhibit highly nonlinear current-voltage characteristics. It is believed that Pr exists at the grain boundaries (GBs) and plays important role for the electrical properties. To better understand the microscopic origin, we have studied the atomic structure and segregation behavior of Pr in ZnO [0001] tilt GBs. Atomic scale GB structure has been widely studied in ceramics and most of the studies have focused only on the major structure. However, GB structure is not entirely the same but there is structural multiplicity. In this study, we have carried out extensive observations of 27.8° (Σ13) and 30.0° tilt GBs. Since these GBs have close tilt angles, their structures are expected to be similar, which allows us to discuss the structural similarity and dissimilarity of these GBs. Furthermore, the atomistic structures will be correlated with the morphology such as facets.

Method

ZnO single GBs were fabricated by bicrystal method, where two ZnO joined by thermal diffusion bonding. To ensure that Pr exists in the GB, a thin layer of Pr metal is deposited on the surface of a ZnO single crystal prior to the bonding. Thin foils for electron microscopy observations were prepared by the conventional technique using mechanical polishing and argon ion beam milling. GBs were observed by transmission electron microscopy (TEM) and high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM). Local chemical composition was measured by energy dispersive X-ray spectroscopy (EDS). In addition, stable GB atomic arrangements of the 27.8° GB was simulated by the first-principles calculations.

Results and discussion

GB plane of the 27.8° tilt GB is almost entirely parallel to $(25\bar{7}0)$. In majority of the area, the GB is described by the zig-zag alignment of structural units (SUs) γ (**Fig. 1 (a)**) [1]. The GB is partially facetted, where the GB plane is nearly parallel to $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ of the adjacent crystals. Unique atomistic structure and Pr segregation pattern forms in the facets. It should be also mentioned that the secondary structure of the $(25\bar{7}0)$ GB plane area form only in the vicinity of facets (**Fig. 1 (b)**). Concentration of Pr is higher in the major structure than in the secondary one, which was verified by EDS.

On the other hand, the boundary plane of the 30.0° tilt GB is parallel to $(38\bar{1}\bar{1}0)$ in most of the area. Here, again, the GB is described by the alignment of SUs γ (**Fig. 1 c**). In the rest of the area, the GB is facetted with the local boundary plane of

$\{10\bar{1}0\}//\{11\bar{2}0\}$. Atomistic structure in this region is quite similar to that in facets of the 27.8° tilt GB. However, no secondary structure is found near facet (**Fig. 1 (d)**). Difference of the tilt angle would lead to different strain state near facets, which may be related with the formation of secondary structure.

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References

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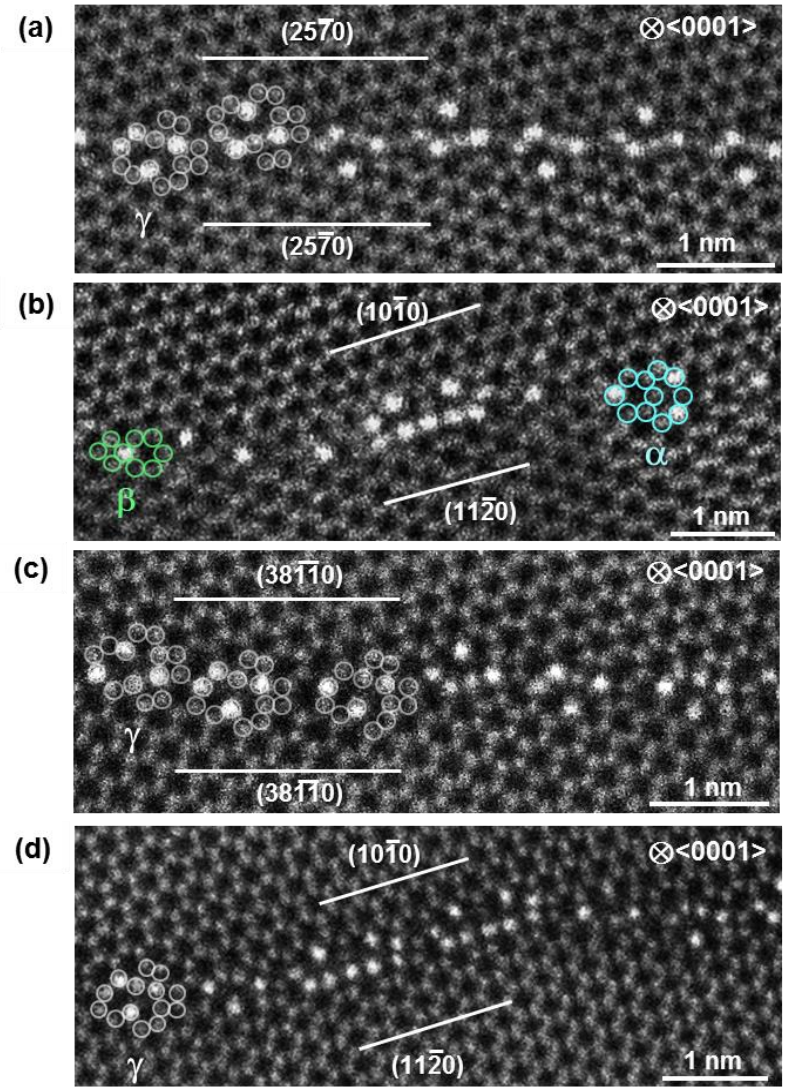

Fig. 1. HAADF-STEM images of the Pr-doped ZnO 27.8° [0001] tilt GB (a) in the (25$\bar{7}$0) boundary plane region and (b) in a facet. HAADF-STEM images of the Pr-doped ZnO 30.0° [0001] tilt GB (c) in the (38$\bar{1}\bar{1}$0) boundary plane region and (d) in a facet. Brightest contrast indicates the location of Pr. SUs (α, β, and γ) are indicated by sets of circles.