論 文 の 内 容 の 要 旨

論文題目　Atomic Arrangement and Segregation Behavior of Praseodymium in Zinc Oxide [0001] Tilt Grain Boundaries

酸化亜鉛[0001]傾角粒界における原子配列およびプラセオジムの偏析挙動

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Zinc oxide (ZnO) has a long history as a material that had been used in the field of material engineering. ZnO is a famous n-type semiconductor with wide band gap of 3.37 eV. Moreover, there have been great developments for obtaining the p-type semiconductivity from the ZnO. ZnO has broad application range including light emitting diodes, transparent electrode, varistors, and sensors. ZnO has advantages of low material cost and the availability of large substrate. When the additives such as dopants or defects are introduced to the polycrystalline ZnO, they affect to the grain boundary geometry or chemistry, and accordingly the performances of the ZnO can be largely changed. In this regard, understanding atomistic structures and distribution of the dopants in the ZnO grain boundary should be carefully investigated. Polycrystalline ZnO doped with Pr exhibit highly nonlinear current-voltage (*I*-*V*) characteristics and being widely used as varistors. It is believed that Pr segregated at the grain boundary promotes formation of native defects (O_i, V_{Zn}) that forms the double Schottky type barrier in the ZnO grain boundary. However, there is huge number of grain boundaries in polycrystalline ZnO, thus, it is practically impossible to determine their atomic structure as well as segregation of Pr.

In this thesis, a systematic investigation of grain boundary is carried out by using bicrystals. Well-defined single ZnO [0001] symmetric tilt boundaries are prepared where two single crystals with have common [0001] axes, and the tilt angle (2θ) made by two $(11\bar{2}0)$ of the adjacent crystals. Here, 2θ ranges from 0° to 60° due to the crystal symmetry, thus controlling 2θ in this range provides a series of the ZnO [0001] tilt grain boundaries. Particularly, the values 2θ are determined to provide coincidence site lattice (CSL) boundary conditions, which are useful for direct observation of atomistic structure by transmission electron microscopy and simulation within realistic computational time with sufficient accuracy. The atomic arrangements of the ZnO CSL boundaries are described by a limited number of elemental structures, which are often described as structure units (SUs).

Grain boundaries fabricated in the bicrystals were analyzed by transmission electron microscopy (TEM) and scanning TEM (STEM). Thin foils for observations are prepared by conventional procedures that include mechanical polishing down to about 30 μm and argon (Ar) ion beam milling for electron transparency. TEM observations were performed using JEM-2010 and JEM-4010 (JEOL Ltd. Tokyo, Japan). STEM observations were carried out using JEM-2100F and ARM-200F, both are equipped with a spherical aberration corrector for the electron probe (CEOS Gmbh, Germany).

Stable GB atomic arrangement has also been explored by theoretical calculation. Three-dimensional periodic boundary conditions can be provided from the CSL boundaries. Atomic arrangement of GB is simulated in two-step methodologies; firstly with static lattice methods with empirical inter-atomic potentials and secondly with the first-principles calculations using VASP program code.

First, atomistic structure of an undoped ZnO symmetric grain boundary is studied in the chapter 3. The investigation was focused on a specific orientation, [0001] Σ13 (32.2°) tilt grain boundary, which is known to form stable atomic arrangements. The grain boundary has two different SU alignments. Dominant structure of the grain boundary was the zig-zag SU alignment, and secondary structure was the straight SU alignment. The results suggest that transition from straight to zig-zag alignment may occur near this orientation. The local configurations of the grain boundary were described in topological description and revealed that both SU alignments are described by edge dislocation core, a= $\frac{1}{3}\langle 11\bar{2}0\rangle$.

In chapter 4, atomistic structure and segregation behavior of Pr-doped ZnO [0001] Σ13 (32.2°) and 30.0° tilt grain boundaries are studied. Common type of SU was found which is also reported from 27.8° tilt grain boundary case (Sato *et al*. Phys. Rev. B (2013)). On the other hand, the locations of Pr were not all the same for the different grain boundaries. This demonstrates that site selectivity of Pr dopant can be varied at different grain boundaries even with the identical SUs. It is suggested that the variation of strain distribution is a cause of change in the location of Pr. Pr has larger ionic size than Zn, it would preferentially substitute the Zn sites with locally largest space.

In the most of grain boundary studies, investigations have been limited to quite narrow boundary area, and only the representative structure is often focused on. However, grain boundary structure is not always that simple; grain boundary plane may not be completely flat, there may be secondary or more structures, steps, facets, and so on. In recent years, stability in electron microscope has been improved, enabling to observe larger area of grain boundary by a quantitative manner. In this regard, a larger area of a ZnO grain boundary is investigated to understand a variety of structures at the atomic scale in chapter 5. Pr-doped ZnO Σ 13 (27.8°) grain boundary is studied that has structural multiplicity in it. Grain boundary is mostly composed of the flat $(25\bar{7}0)$ boundary area and partly of facets that are almost parallel to $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ of the adjacent crystals. There is strain field near facets to enhance Pr segregation. And the secondary structure is locally preferred near the facet, where Pr concentration is lowered. Thus, it is considered that segregation at the grain boundary affects to the local atomic arrangements. Topological analysis successfully characterized the local atomic configurations as well as DSC step dislocation. The step may lead to formation of the secondary structure by displacement of the boundary plane.

Finally in chapter 6, atomic arrangements with SU description, segregation of Pr are more generalized. As will be introduced in the previous chapters, atomic arrangement and Pr segregations in a series of ZnO grain boundaries are studied. Those give an idea for understanding 2θ dependency for Pr-doped ZnO [0001] symmetric tilt grain boundaries. SU arrangements of low-ΣCSL boundaries (Σ49 (16.4°/43.6°), Σ7 (21.8°/38.2°), and Σ13 (27.8°/32.2°)) and non-low-Σ CSL boundaries (near Σ97(30.0°), and near Σ79(25.8°)) grain boundaries were studied that roughly cover overall 2θ range ($0° < 2\theta < 60°$). Several trends have been found; Most of the grain boundaries consist of SUs α, β, or γ. The SUs

transformation between the SU α/β and SU γ were found at the grain boundaries with 2θ near 30.0°. During the structure transition, SUs coexist in the boundary whether periodically or randomly. SU arrangements can be expressed as inter-mixed configuration by the SUs of neighbored grain boundaries. Since each type of SU has specific number of Pr sites within it, concentration of Pr is considered to be the highest when 2θ of grain boundary is close to 30°.