論文の内容の要旨

Abstract of Dissertation

Atomic and Electronic Structure of Grain Boundaries in $SrTiO_3$

($SrTiO_3$粒界の原子および電子構造)

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Abstract

The characterization of grain boundary (GB) in atomic level is essential to understand and design the materials. It is well-known that the materials properties of GB are not same as that in bulk. Also, in the case of ceramics, the chemical composition in the vicinity of GB is different to bulk and the imperfection of bonding structure at GB core usually provides more vacancies than at bulk. In addition, GB core structure provides the faster mass transfer path, which gives high diffusion coefficient at GB. The atomic structure in the vicinity of GB plays an important role to understand the nonstoichiometry and the diffusion behavior at GB.

On the other hand, a systematic study on the atomic structures of GBs in engineering materials is difficult to perform because GB structure could not be controlled properly in polycrystalline and GB morphology changes dramatically with heat-treatment condition. Therefore, the bicrystal method has been extensively studied to characterize the atomic structure of GB in various materials. The bicrystal consists of two single crystals intentionally oriented. In addition, recent advents on the characterization technique such as Scanning Transmission Electron Microscopy (STEM) made it possible to characterize the atomic structure of GBs with the support of first principles calculation.

Especially, the atomic structure of GBs in $SrTiO_3$ has been studied extensively because it is a cubic Perovskite structure with high symmetry and two different cations, Sr and Ti, of which the atomic columns are distinguishable in a high-angle annular dark-field (HAADF)-STEM method. In addition, $SrTiO_3$ is one of important electroceramic materials used as capacitors and low-voltage varistor. In this material, it was reported that the electrical property such as non-linear I-V characteristics strongly depends on GB structures. Moreover, it was suggested that the electronic properties and the nonstoichiometry at GB are correlated to the morphology of the GB. Therefore, the characterization of the atomic structures of the GB and the relationships with the GB morphology are important for further understanding and finding the way to control the material's properties

Due to its importance, the atomic structures and nonstoichiometry of $SrTiO_3$ symmetric tilt GBs

have been extensively studied by combining bicrystal experiments, high resolution microscopy, and theoretical calculations. Ti excess near GB plane in Perovskite materials compared to bulk was reported in many literatures and it was believed that nonstoichiometry at GB was related to GB electronic property. However, the relationship between GB structure and nonstoichiometry was not fully understood. In Chapter 3, for understanding the chemical composition at GB in $SrTiO_3$, defect energetics in nonstoichiometry in four model symmetric tilt GBs, [110](111)Σ3, [001](210)Σ5, [001](510)Σ13 A and [001](510)Σ13 B, are discussed. . Examining the chemical composition with STEM-EDS methods and calculations of defect energetics in model boundaries systematically, the nonstoichiometry in the vicinity of GB is examined and discussed energetically. It is found that the change of chemical composition could be understood by the difference of defect energetics

Although a number of studies on the atomic structure of GB in $SrTiO_3$ have been reported, most studies focused on the characterization of symmetric tilt GBs while the characterization of asymmetric tilt GBs has not been studied yet. This is due to the difficulties to make the proper model structures of the asymmetric tilt GB and the hardness to characterize the atomic structure at GB core with the conventional approaches. V. Randle reported that the microstructure could not compose of only symmetric tilt GB and the most observed boundaries were asymmetric tilt GB expect [110](111)Σ3 by observing the microstructure of Ni grains. Moreover, the impact of asymmetric tilt GBs was more effective to GB electrical properties than symmetric tilt GBs with the similar misorienetation angle in $SrTiO_3$. Thus, the study on the asymmetric tilt GBs is necessary to apply bicrystal experiments to the engineering materials which contain a number of GBs. Modeling the asymmetric tilt GB with the help of simple geometry, the atomic structure of the asymmetric tilt GB, [001](100)//(430) is examined theoretically and experimentally in Chapter 4. Four model structures with different terminations, Sr-Sr, Sr-Ti, Ti-Sr and Ti-Ti, were considered and HAADF-STEM characterization in [001](100)//(430) bicrystal was also performed. It was found that the atomic structure of Ti-Ti termination were in good agreement with the observed structure. In addition, GB energy of [001](100)//(430) was related to the chemical potential of each element and that could be achieved in $1.0J/m^2$, which is almost same as the symmetric tilt GB, [001](210)Σ5 and [001](310)Σ5. Before this study, GB energies of the asymmetric tilt GB were considered as around $2.0J/m^2$ and these GBs were regarded as the unstable GB.

Furthermore, GB morphology in atomic level is also necessary to understand GB. It was reported that the microstructure of polycrystalline ceramics GB morphology depends on sintering condition and the material's properties also changed dramatically. However, GB morphology change of $SrTiO_3$ in atomic level has not been studied yet. In Chapter 5, based on the calculated GB energy (in Chapter 3 and Chapter 4) and model experiments, the effect of temperature and atmosphere on GB morphology in the asymmetric tilt bicrystal is examined and discussed in the atomic in the atomic level. The asymmetric tilt [001] (100)//(430) bicrystal consists of two symmetric tilt GBs and one asymmetric tilt GB. The length and portion of each GB structure changed with heat-treatment was

investigated. In order to examine the effect of temperature on GB morphology, the samples heat-treated in 1450°C, 1600°C and 1650°C air for 120hr were prepared. The experimental results is discussed with the change of anisotropy in GB energies and GB migration. Moreover, the sample heat-treated in 5% H_2-95% Ar on 1450°C for 120hr were prepared to examine the effect of atmosphere. With heat-treatment in reducing atmosphere, the chemical potential of each element is also changed. The morphology change with heat-treatment could be understood by GB energetics of [001](100)//(430) Ti-Ti termination in different equilibrium conditions. This study shows the possibility to understand and predict GB morphology thermodynamically if GB energies of structures consisting GB morphology are calculated.

In $SrTiO_3$, the electronic structure is also important to understand materials properties. Therefore, the electronic structure at each model GB was evaluated in Chapter 6. Recently, it was reported that the GB-induced unoccupied state formed and changed materials' properties in MgO GB. Similar, the extra state due to GB, which reduces band gap apparently, was examined in the model GBs, the electronic structure of each GB was examined to understand electronic properties at GB. Examining the band gap of each GB systematically, the relationship between atomic structure and electronic structure of GB is investigated. The GB-induced unoccupied states was found within bandgap. Moreover, the square of wave functions in the GB-induced level was illustrated. Interestingly, in the asymmetric tilt GB, [001](100)//(430), the localization of electrons at the specific Ti sites was calculated and it would be related to the distortion of bonding structure at GB core. The relationship between the electronic structure and the material's properties is also discussed.

Moreover, in Chapter 7, the case study for the geometric method to model the asymmetric tilt GB model was introduced. In order to confirm the geometric modeling for asymmetric tilt GB, two additional bicrystals satisfying Pell's number, [110](221)//(001) and [110](114)//(110), were prepared and these boundaries were calculated. It was found that the atomic structure of [110](221)//(001) was characterized and the newly introduced GB, [110](225)//(441), was found in [110](114)//(110) bicrystal. The geometric relationship and GB energetics in [110](114)//(110) bicrystal was discussed and the atomic structure of [110](225)//(441) were characterized. This results shows that the geometrically prepared bicrystal gives a chance to find the stable asymmetric or symmetric tilt GB structures, which are essential to extend our understanding of GB and make it possible to predict GB morphology.

In this study, the atomic structures, nonstoichiometry and GB morphology of model $SrTiO_3$ GBs, including both symmetric and asymmetric tilt GBs, are systematically investigated by using aberration corrected (STEM) and first principles calculations to understand $SrTiO_3$ GBs further. The atomic structures of three symmetric tilt GB structures, [110](111)Σ3, [001](210)Σ5 and [001](510)Σ13, and three asymmetric tilt GB structures, [001](100)//(430), [110](221)//(001) and [110](225)//(441) are discussed. The atomic models of asymmetric tilt GBs, which are important but

not examined yet, were constructed with the help of geometric consideration, Pythagoras's triangle and Pell's number. In addition, the other important issues in understanding GB such as the chemical composition at GB and GB morphology are also discussed. Finally, in the case study, with the proposed the modeling methods for the asymmetric tilt GB, it is success to characterize the new asymmetric tilt GB, which has not been reported within author's knowledge. This indicated that the basic GB structures, which are necessary to understand GB phenomena, could be found in this approach and these GB structures make the further understanding of GB structure possible.

Based on the results presented in this thesis, a general conclusion can be given: the atomic and electronic structures of $SrTiO_3$ GBs could be achieved with the combination of calculation and experiment with a help of the geometric consideration. Moreover, the chemical composition at GB and GB morphology, which is essential to predict GB properties, could be understood energetically.