

Abstract (論文の内容の要旨)

論文題目 Inversion Domain Boundaries in ZnO: Atomic-Scale Structural and Elemental Analysis, Electronic Structure Calculations and Thermoelectric Properties
(酸化亜鉛における反転ドメイン境界の原子・電子構造および熱電特性に関する研究)

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In this thesis, the results of the investigation of the atomistic and electronic properties of inversion domain boundaries (IDB) in ZnO have been reported. The Mn-Al and Sn-Al dual-doped ZnO systems have been studied and the microstructural features that develop upon doping have been characterized using experimental methods including X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS). Using atomic-resolution annular bright-field (ABF) and high-angle annular dark-field (HAADF) STEM, the structural properties of the IDB interfaces that form in $\text{Zn}_{0.89}\text{Mn}_{0.1}\text{Al}_{0.01}\text{O}$ and $\text{Zn}_{0.98}\text{Sn}_{0.01}\text{Al}_{0.01}\text{O}$ have analyzed at the atomic level. Based on the observed structural features of the IDBs and the IDB chemical composition, determined by EDS and EELS analysis, slab model structures representative of the experimentally observed IDB interfaces have been constructed and structural refinement has been carried out using first principles density functional theory (DFT) calculations. The local atomistic and electronic properties of the refined IDB models have been analyzed. Finally, the thermoelectric properties of the Mn-Al and Sn-Al dual-doped ZnO ceramic materials synthesized have been studied, with measurements of the electrical conductivity, Seebeck coefficient and thermal conductivity being carried out from room temperature to $\sim 750^\circ\text{C}$. The results of thermoelectric property measurements have been discussed in terms of the specific influences of varying the dopant concentration and of the formation of IDBs on the thermoelectric properties.

Chapter 1 includes a description of the crystallographic properties of ZnO, the $\text{RMO}_3(\text{ZnO})_n$ homologous phase compounds in which inversion domain (ID) network formation occurs, and the ZnO-based spinel phases. Emphasis is placed on the description of the influence of doping on the structural and functional properties of ZnO-based materials. The basic properties of thermoelectric materials, particularly oxide thermoelectrics materials such as ZnO, are also described. The chapter is concluded by an explanation of the motivation for the study, i.e. to investigate the influence of multiple-dopant addition on the microstructural and thermoelectric properties of ZnO-based ceramic

materials. In chapter 2, the experimental methods used for the synthesis and characterization of the materials studied in this work are described in detail. Among the experimental methods described are XRD, SEM, TEM, ABF/HAADF-STEM, EDS and EELS. The basic theory underlying the density functional theory, which has been used for the refinement and analysis of IDB interfaces, is also explained. Lastly, the experimental methods used for the measurement of the thermoelectric properties of Mn-Al and Sn-Al dual-doped ZnO ceramic samples are described.

In Chapter 3, the results of the phase and microstructural analysis, by XRD, SEM and TEM, of ZnO ceramic samples co-doped with Al (1 at. %) and Mn (0, 1, 2, 5 and 10 at. %) and sintered at 1400°C for 12 h in air are described. As the Mn concentration increases, an increase of the lattice parameter of ZnO is observed, indicating the substitution of Mn on the Zn sublattice. XRD profile analysis also indicated the formation of spinel secondary phases. The 10 at. % Mn doped sample ($\text{Zn}_{0.89}\text{Mn}_{0.1}\text{Al}_{0.01}\text{O}$) exhibited a microstructure consisting of defects, as indicated by the broadening of the (002) ZnO peak in the XRD profile. Microstructure observation of $\text{Zn}_{0.89}\text{Mn}_{0.1}\text{Al}_{0.01}\text{O}$ by bright-field (BF) and dark-field (DF) TEM confirmed that the peak broadening was due to the formation of ID networks within individual grains. The significant concentration of Mn (10 at. %) in $\text{Zn}_{0.89}\text{Mn}_{0.1}\text{Al}_{0.01}\text{O}$, exceeding the solubility limit of Mn in ZnO, is considered to contribute to the formation of the ID networks observed. To investigate the structural and chemical composition of the IDB interfaces within the ID networks, ABF/HAADF-STEM and STEM-EDS/EELS analysis of the basal-plane IDB (b-IDB) was carried out. It was determined by ABF/HAADF-STEM observation that a head-to-head (H-H) configuration of the c-axis forms at the b-IDB interface; in addition, a c-axis stacking fault (SF) was also observed at the b-IDB interface, with a local c-axis cation stacking sequence of $\alpha\beta\alpha\beta|\gamma|\alpha\beta\alpha\beta$ observed at the b-IDB. STEM-EDS analysis confirmed a significant increase of the Mn concentration and a minor increase of the Al concentration at the b-IDB interface, indicating the localization of both dopants at the b-IDB, while STEM-EELS revealed a significant increase of the Mn-L_{2,3} signal exactly at the b-IDB cation layer, demonstrating that the localization of Mn occurs primarily within the single cation layer composing the b-IDB interface.

In Chapter 4, the phase and microstructural properties of the Sn-Al dual-doped ZnO ceramics ($\text{Zn}_{0.98}\text{Sn}_{0.01}\text{Al}_{0.01}\text{O}$) sintered at 1400°C for 12 h in air are described. Comparisons are also made with ZnO ceramics doped with either Sn or Al only ($\text{Zn}_{0.99}\text{Sn}_{0.01}\text{O}$ and $\text{Zn}_{0.99}\text{Al}_{0.01}\text{O}$). XRD profile analysis of $\text{Zn}_{0.98}\text{Sn}_{0.01}\text{Al}_{0.01}\text{O}$ indicated that, in contrast to $\text{Zn}_{0.99}\text{Sn}_{0.01}\text{O}$ and $\text{Zn}_{0.99}\text{Al}_{0.01}\text{O}$, in which ZnAl_2O_4 and Zn_2SnO_4 spinel phases formed respectively, spinel phase formation did not occur. In addition, a low-intensity additional peak, likely representing a superlattice reflection due to a structural modulation, was observed near the (002) ZnO peak and several ZnO peaks exhibited broadening, indicative of defect formation, in the XRD profile of $\text{Zn}_{0.98}\text{Sn}_{0.01}\text{Al}_{0.01}\text{O}$. To investigate the microstructural origin of the unique features of the XRD profile of $\text{Zn}_{0.98}\text{Sn}_{0.01}\text{Al}_{0.01}\text{O}$ further, SEM and TEM analysis was carried out. SEM observation revealed that spinel phase precipitates did not form within the microstructure of $\text{Zn}_{0.98}\text{Sn}_{0.01}\text{Al}_{0.01}\text{O}$, while BF-TEM demonstrated the presence of intergrowth-like features within individual grains. DF-TEM analysis of the intergrowth-like features confirmed them to be ID networks. These features were observed throughout essentially all grains

observed in $\text{Zn}_{0.98}\text{Sn}_{0.01}\text{Al}_{0.01}\text{O}$ samples, with no spinel precipitates being observed. To analyze the IDB interfaces in the ID networks at a higher resolution, ABF/HAADF-STEM and STEM-EDS/EELS analysis was carried out. STEM-EDS analysis of the ID networks demonstrated that the Sn and Al dopants localize primarily at the respective interfaces of the b-IDB and pyramidal-plane IDB (p-IDB) interfaces respectively. Atomic-resolution ABF/HAADF-STEM analysis of the b-IDB further indicated a significant concentration of Sn within the cation monolayer at the b-IDB. This was also confirmed by STEM-EELS point analysis of the b-IDB interface, with the observation of an O K edge resembling that consistent with known tin oxide compounds. ABF/HAADF-STEM analysis of the p-IDB interface indicated that in contrast to the b-IDB, which essentially consists of a cation monolayer, the p-IDB is several atomic columns wide. Based on ABF-STEM image analysis, it was also confirmed that H-H and tail-to-tail (T-T) configurations of the c-axis form at the b-IDB and p-IDB interfaces respectively. The finding that spinel phase formation does not occur in $\text{Zn}_{0.98}\text{Sn}_{0.01}\text{Al}_{0.01}\text{O}$, with, instead, the formation of ID networks stabilized by the localization of Sn and Al at the respective b-IDB and p-IDB interfaces occurring, despite the reverse, i.e. spinel phase formation without ID network formation, occurring in $\text{Zn}_{0.99}\text{Sn}_{0.01}\text{O}$ and $\text{Zn}_{0.99}\text{Al}_{0.01}\text{O}$, is unusual and has potential implications for the synthesis of yet unidentified $\text{RMO}_3(\text{ZnO})_n$ homologous phase compounds, where R and M are the dopants occupying the b-IDB and p-IDB sites respectively, which may be stabilized based on the localization of specific dopants at the distinct sites of the b-IDBs and p-IDBs. Two important factors which may contribute to the ability of specific dopants to occupy either the five-fold p-IDB or octahedral b-IDB sites are the dopant ionic radius and stable valence state. These as well as other factors which may contribute to the ability of certain dopants to occupy the b-IDB and/or p-IDB sites and, thus, to stabilize the formation of ID networks in ZnO ceramics, have been discussed in detail.

Chapter 5 includes the results of structural refinement by first principles DFT calculations of models of the Mn-doped and Sn-doped b-IDB interfaces that were characterized by atomic-resolution ABF/HAADF-STEM. Slab models containing a single b-IDB interface, consisting of a monolayer of either the Mn or Sn dopants, were constructed and structural refinement was carried out. The local atomistic structure of the Mn-doped b-IDB exhibits a structure in agreement with that observed experimentally, with a c-axis cation stacking sequence of $\alpha\beta\alpha\beta|\gamma|\alpha\beta\alpha\beta$. The local electronic density of states (DOS) at the Mn-doped b-IDB exhibited hybridized Mn d and O p states within the valence band and localized Mn d states within the conduction band, with the appearance of such features attributed to the local octahedral coordination environment of Mn at the b-IDB. The refined Sn-doped b-IDB slab model interface contained two distinct Sn sites, Sn1 and Sn2, with Sn-O bond lengths resembling those of Sn^{2+} and Sn^{4+} in the SnO and SnO₂ compounds respectively. It is possible that the local structure of the Sn-doped b-IDB relaxes to assume an atomic configuration with distinct Sn sites in order to achieve a local average cation valence state of 3+, which is a necessary condition for maintaining electrostatic neutrality at the b-IDB interface. The local DOS at the Sn-doped b-IDB exhibited a significant reduction in the fundamental band gap magnitude, to a value of 0.72 eV, compared to the value of 2.23 eV for bulk ZnO, determined using similar calculational parameters. The reduction in the fundamental band gap is

attributed to the close proximity of the Sn s states to the conduction band minimum of ZnO, which results in a renormalization of the band gap due to the hybridization of the Sn s states with the conduction band states of ZnO.

In Chapter 6, the results of thermoelectric property measurements of the Mn-Al and Sn-Al dual-doped ZnO ceramics are presented. The electrical conductivity (σ), Seebeck coefficient (S) and thermal conductivity (κ) have been measured and, using these measured values, the thermoelectric power factor and figure of merit (ZT) were calculated. The addition of Al to ZnO resulted in a significant increase of the σ values and produced an electrical conductivity exhibiting a metallic character. The addition of increasing concentrations of Mn to ZnO resulted in a gradual decrease of σ due to point defect scattering caused by the substitution of Mn on the Zn sublattice, while, simultaneously, the character of σ shifted to exhibit an increasingly activated or semiconducting character. The $\text{Zn}_{0.89}\text{Mn}_{0.1}\text{Al}_{0.01}\text{O}$ and $\text{Zn}_{0.98}\text{Sn}_{0.01}\text{Al}_{0.01}\text{O}$ samples, which contain IDBs, exhibited the most strongly activated character of σ , likely due to the presence of IDBs, which may act as electronic potential energy barriers. The addition of Mn, up to a concentration of 5 at. %, resulted in no significant change in the Seebeck coefficient magnitude, $|S|$, in comparison to $\text{Zn}_{0.99}\text{Al}_{0.01}\text{O}$. This is attributed to the fact that Mn likely substitutes for Zn^{2+} in the 2+ state, resulting in minimal change in the carrier density. However, at the 10 at. % Mn doping level, a significant increase in $|S|$ was observed over the measured range of temperatures. Similar temperature-dependent behavior and values of $|S|$ were obtained for the $\text{Zn}_{0.98}\text{Sn}_{0.01}\text{Al}_{0.01}\text{O}$ sample. The increase in the values of $|S|$ in the samples containing IDBs can be attributed the modification of the local electronic structure at the IDB interfaces, which may result in electron filtering, in the case of the formation of potential barriers, or in increases in the local DOS due to electron trapping or localization, which may occur in the case of quantum well formation. Either of these phenomena could contribute to the increase of $|S|$. Lastly, the addition of increasing concentrations of Mn resulted in the gradual reduction of κ , due to increasing point-defect scattering of phonons caused by the substitution of Mn^{2+} for Zn^{2+} on the Zn sublattice. At the doping level of 10 at. % Mn, the formation of IDBs appeared to result in a significant, additional decrease in the values of κ throughout the measured range of temperatures, likely as a consequence of the scattering of phonons at the IDB interfaces, with an average c-axis spacing between neighboring b-IDBs of ~ 50 nm. In $\text{Zn}_{0.98}\text{Sn}_{0.01}\text{Al}_{0.01}\text{O}$, values of κ similar to those in $\text{Zn}_{0.89}\text{Mn}_{0.1}\text{Al}_{0.01}\text{O}$ were observed throughout the measured range of temperatures, despite the lack of a significant concentration of point defects. The smaller average c-axis spacing between neighboring b-IDBs, ~ 15 nm in $\text{Zn}_{0.98}\text{Sn}_{0.01}\text{Al}_{0.01}\text{O}$, appears to account for the additional drop in κ in this sample.

The thesis is concluded by Chapter 7, in which the results are summarized and the possible implications of the findings are discussed in terms of their applicability to potential future investigations.