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論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

This thesis is entitled "First-Principles Study on Electronic Structure and Doping for Novel Compound Semiconductors, $BaZn_2As_2$, SnS, and Cs_2SnI_6" and consists of 8 chapters.

In **Chapter 1 "General Introduction,"** the background and objective of this study are described.

In **Chapter 2 "High-Mobility *p*-Type Amorphous Semiconductor $BaZn_2As_2$,"** amorphous $BaZn_2As_2$ (a-$BaZn_2As_2$) thin films were fabricated by pulsed laser deposition (PLD). The structural, optical, and electrical properites of a-$BaZn_2As_2$ were investiaged. It was found that the a-$BaZn_2As_2$ films exhibited band gaps of > 1.04 eV and *p*-type conduction with high hole mobilities ~10 $cm^2\ V^{-1}\ s^{-1}$. Further, epitaxial β-$BaZn_2As_2$ films were grown by a reactive solid-phase epitaxy method. The β-$BaZn_2As_2$ films exhibited high crystalline quality, but unexpectedly a narrow band gap of 0.23 eV.

In **Chapter 3 "Chemical Origins of the Narrow Band Gap in β-$BaZn_2As_2$"** the origins of narrow band gap in β-$BaZn_2As_2$ were studied in comparison with a similar compound LaZnAsO with a larger band gap (1.5 eV) based on the chemical bonding analyses probed by 6 keV hard X-ray photoemission spectroscopy, hybrid density functional theory (DFT) calculations, and the ligand theory. One origin is the direct As-As hybridization between adjacent [ZnAs] layers, which leads to a secondary splitting of As 4*p* levels and raises the VBM. The other is that the non-bonding Ba $5d_{x2-y2}$ orbitals form unexpectedly deep conduction band minimum (CBM) in β-$BaZn_2As_2$ although the CBM of LaZnAsO is formed mainly of Zn 4*s*. These two origins provide a quantitative explanation for the bandgap difference between β-$BaZn_2As_2$ and LaZnAsO.

In **Chapter 4 "Origins of Doping Asymmetry in SnS,"** Defect formation and doping mechanism were studied for SnS by DFT. The native *p*-type conduction in SnS is originated mainly from Sn vacancies. It is difficult to dope SnS *n*-type because the shallow acceptor Sn vacancy forms readily and largely at *n*-type conditions, which compensente *n*-type doping sources. The origins of the doping asymmetry in SnS is explained by its too shallow VBM and CBM levels, i.e., too small ionization potential and electron affinity, which are caused by the strong *s*–*p* and *p*–*p* couplings between Sn^{2+} cation and S^{2-} anion, respectively. Further, Sb and Bi doping in SnS was assessed and found not effective to attain *n*-type conduction in SnS.

In **Chapter 5 "*n*-Type Conversion of SnS by Geometrical Doping Route,"** carrier polarity conversion to *n*-type was achieved by isovalent ion substitution for polycrystalline SnS thin films on glass substrates. Substituting Pb^{2+} for Sn^{2+} converted the majority carrier

from hole to electron, and the free electron density ranged from 10^{12} to 10^{15} cm^{-3} with the largest electron mobility of 7.0 $cm^2/(Vs)$. The *n*-type conduction was confirmed further by the position of the Fermi level (E_F) based on photoemission spectroscopy and electrical characteristics of pn heterojunctions. Density functional theory calculations reveal that the Pb substitution invokes a geometrical size effect that enlarges the interlayer distance and subsequently reduces the formation energies of Sn and Pb interstitials, which results in the electron doping.

In **Chapter 6 "Electronic Structure of a Perovskite Variant Cs_2SnI_6,"** the electronic structure of a recently-reported perovskite variant, Cs_2SnI_6, was studied by hybrid DFT calculations. The real oxidation state of Sn in Cs_2SnI_6 was revealed closer to +2 similar to that in $CsSnI_3$, not +4 expected from a simple ionic model of $Cs^{+}_2Sn^{4+}I^{-}_6$. The +2 oxidation state of Sn originates from 2 ligand holes ($\underline{L}^{+}$) in the $[SnI_6]^{2-}$ octahedron unit, where the ligand $[I_6]$ cluster has the apparent $[I_6^{6-}\underline{L}^{+}_2]^{4-}$ oxidation state, because the band gap is formed mainly by occupied I 5*p* VBM and unoccupied I 5*p* CBM. The +2 oxidation state of Sn and the band gap originates from the intracluster hybridization and stabilized by the strong covalency of the Sn–I bonds.

In **Chapter 7 "Intrinsic Defects in a Perovskite Variant Cs_2SnI_6,"** intrinsic defects in Cs_2SnI_6 were investigated using hybrid DFT calculations. It is revealed that iodine vacancy and tin interstitial are the dominant defects that are responsible for the intrinsic *n*-type conduction in Cs_2SnI_6. Tin vacancy has a very high formation energy (>3.6 eV) due to the strong covalency in the Sn–I bonds and is hardly generated for *p*-type doping. All the dominant defects in Cs_2SnI_6 have deep transition levels in the band gap and can be suppressed significantly by employing an I-rich synthesis condition, which is inevitable for photovoltaic and other semiconductor applications.

In **Chapter 8 "General Conclusions,"** this study is summarized, and future perspective is described.