

論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	First-Principles Study on Electronic Structure and Doping for Novel Compound Semiconductors, BaZn ₂ As ₂ , SnS, and Cs ₂ SnI ₆
著者(和文)	XiaoZewen
Author(English)	Zewen Xiao
出典(和文)	学位:博士(理学), 学位授与機関:東京工業大学, 報告番号:甲第9957号, 授与年月日:2015年9月25日, 学位の種別:課程博士, 審査員:神谷 利夫, 多田 朋史, 東 正樹, 細野 秀雄, 大場 史康, 平松 秀典
Citation(English)	Degree:, Conferring organization: Tokyo Institute of Technology, Report number:甲第9957号, Conferred date:2015/9/25, Degree Type:Course doctor, Examiner:
学位種別(和文)	博士論文
Type(English)	Doctoral Thesis

**First-Principles Study on Electronic Structure and
Doping for Novel Compound Semiconductors,
BaZn₂As₂, SnS, and Cs₂SnI₆**



Zewen Xiao

Department of Innovative and Engineered Materials

Tokyo Institute of Technology

2015

Contents

Chapter1 General Introduction	1
1.1 Background of This Study	1
1.1.1 Band Aligment of Inorganic Semiconductors	1
1.1.2 Chemical Design of Inorganic Semiconductors	2
1.1.3 Doping Asymmetry in Inorganic Semiconductors	5
1.2 Objectives of This Study	7
1.3 Outline of the Thesis	8
References	10
Chapter 2 High-Mobility <i>p</i>-Type Amorphous Semiconductor BaZn₂As₂	15
2.1 Introduction	15
2.2 Experimental and Computational Details	17
2.2.1 Target Fabrication	17
2.2.2 Thin Film Growth	18
2.2.3 Characterization	18
2.3 Results and Discussion	19
2.3.1 Structural Properties of Amorphous BaZn ₂ As ₂ Films	19
2.3.2 Optical Properties of Amorphous BaZn ₂ As ₂ Films	20
2.3.3 Electrical Properties of Amorphous BaZn ₂ As ₂ Films	20
2.3.4 Epitaxial Growth and Narrow Band Gap of Crystalline β -BaZn ₂ As ₂	21
2.4 Conclusions	23
References	23
Chapter 3 Chemical Origins of the Narrow Band Gap in β-BaZn₂As₂	30
3.1 Introduction	30
3.2 Computational Details	32
3.3 Results and Discussion	33
3.3.1 Crystal Structure Difference between β -BaZn ₂ As ₂ and LaZnAsO	33
3.3.2 Electronic Structure Differences between β -BaZn ₂ As ₂ and LaZnAsO	33
3.3.3 Origins of the Narrow Band Gap: I. Interlayer As–As Hybridization	35
3.3.4 Origins of the Narrow Band Gap: II. Nonbonding Ba 5 <i>d</i> _{<i>x</i>²–<i>y</i>²} Orbital	36

3.4 Conclusions	37
References	37
Chapter 4 Origins of Doping Asymmetry in SnS.....	46
4.1 Introduction	46
4.2 Computational Details	48
4.3 Results and Discussion	49
4.3.1 Properties of Intrinsic Defects in SnS	49
4.3.2 Origins of Doping Asymmetry in SnS	50
4.3.3 Assessment of Sb ³⁺ and Bi ³⁺ Doping in SnS	53
4.4 Conclusions	54
References	54
Chapter 5 <i>n</i>-Type Conversion of SnS by Geometrical Doping Route.....	61
5.1 Introduction	61
5.2 Experimental and Computational Details	62
5.2.1 Fabrication and Characterization	62
5.2.2 Theoretical Calculations	63
5.3 Results and Discussion	63
5.3.1 Structural properties of (Sn _{1-x} Pb _x)S films	63
5.3.2 Electrical Properties of (Sn _{1-x} Pb _x)S films	64
5.3.3 Electronic Structure and Band Alignment of (Sn _{0.5} Pb _{0.5})S	66
5.3.4 Microscopic Mechanism of <i>n</i> -Type Doping by Pb Substitution	68
5.4 Conclusions	70
References	70
Chapter 6 Electronic Structure of a Perovskite Variant Cs₂SnI₆	76
6.1 Introduction	76
6.2 Computational Details	78
6.3 Results and Discussion	79
6.3.1 Crystal and Electronic Structures of Cs ₂ SnI ₆	79
6.3.2 Oxidation State of Sn in Cs ₂ SnI ₆	80
6.3.3 Bonding Nature and Origin of Band Gap in Cs ₂ SnI ₆	81
6.4 Conclusions	83
References	84

Chapter 7 Intrinsic Defects in a Perovskite Variant Cs₂SnI₆	93
7.1 Introduction	93
7.2 Computational Details	94
7.3 Results and Discussion	96
7.3.1 Properties of Intrinsic Defects in Cs ₂ SnI ₆	96
7.3.2 Origins of Deep Defect Levels in Cs ₂ SnI ₆	97
7.4 Conclusions	100
References	100
Chapter 8 General Conclusions	107
8.1 General Conclusions	107
8.2 Future Perspective	108
Acknowledgements	110
Publication List	112
Papers Included in the Thesis	112
Other Papers	113
Presentation List	114
International Oral Presentations	114
International Poster Presentations	114
Demotic Poster Presentations	115

Chapter 1

General Introduction

1.1 Background of This Study

1.1.1 Band Alignment of Inorganic Semiconductors

Novel compound semiconductors exhibit a wide variety of electronic functions and are expected to take over the current silicon technology for some applications. Controlling both *n*-type and *p*-type conductivities in a semiconductor is very important for some practical semiconductor devices such as *p/n* junctions and *p/i/n* light-emitting diodes/solar cells. However, doping asymmetry is a serious issue in some compound semiconductors with strong ionicity, where only either of *n*-type or *p*-type doping is realized.

The dopability of semiconductors can be empirically understood based on the band alignment of various semiconductors, e.g., as shown in Fig. 1.1. A semiconductor cannot easily be doped *n*-type if its conduction band minimum (CBM) lies too shallow towards the vacuum level (E_{vac}), i.e., its electron affinity (*EA*) is too small. CuAlO_2 would be an example. On the other hand, a semiconductor cannot easily doped *p*-type if its valence band maximum (VBM) lies too deep from the E_{vac} , i.e., the ionization potential (*IP*) is too large. Most oxides such as ZnO are typical examples. Besides, the band alignment is also often practically used to design a wide variety of semiconductor devices, heterojunctions, etc.

1.1.2 Chemical Design of Inorganic Semiconductors

Inorganic solids with wide band gaps are usually classified as electrical insulator and are used in industry as electrical insulators, dielectrics, and optical materials. Many metal oxides have wide band gaps because of the significant contribution of ionic character to the chemical bonds between metal cations and oxygen anions. The ionic nature simultaneously suppresses the formation of easily ionizable shallow donors or acceptors and tends to cause the localization of electrons and holes. Exceptionally, some wide band gap oxides are conductive [1,2]. The oxides of *p*-block heavy-metal cations with $(n-1)d^{10}ns^0$ electron configurations (where principal quantum number $n > 4$)—such as ZnO, Ca₂O₃, In₂O₃, SnO₂, and their complex compounds/solid solutions (see Fig. 1.1)—can be converted to *n*-type conductors by electron doping with keeping the optical transparency for human eyes. Transparent conducting oxides (TCOs), represented by commercially available Sn-doped In₂O₃ (indium tin oxide, ITO), have widely been used as transparent electrodes for liquid crystal displays (LCDs), organic light-emitting diodes (OLEDs), electrochromic windows, and solar cells [3,4]. In these ionic oxides, their CBM are composed primarily of unoccupied *s* orbitals of the *p*-block heavy metal cations. The spatial spread of the unoccupied *s* orbitals is so large that the direct overlap between the *s* orbitals of adjacent cations is possible and the effective electron mass is small. As a result, TCOs exhibit high electron mobilities, e.g. $>150 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for In₂O₃ [5].

In 1996 Prof. Hosono proposed a working hypothesis for exploring transparent conducting amorphous oxides [6]. In the hypothesis, the magnitude of the overlap of neighboring *p*-block metal *ns* orbitals was considered insensitive to disordered metal–oxygen–metal (M–O–M) chemical bonds that intrinsically exist in amorphous materials because of the isotropic shape of *s* orbitals [7], and therefore the amorphous

oxides would have high electron mobility comparable to that in the corresponding crystalline phase. This simple hypothesis have been proved valid and useful by the observation of high electron mobilities $\sim 10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in amorphous Cd_2GeO_4 , AgSbO_3 and Cd_2PbO_4 [6]. In 2004, Hosono group [8] reported transparent and flexible thin-film transistors (TFTs) using amorphous In–Ga–Zn–O (a-IGZO), a representative amorphous oxide semiconductors (AOSs), which have advantages such as optical transparency and high electron mobilities $> 10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ over conventional amorphous semiconductors such as hydrogenated amorphous silicon (a-Si:H) [9]. Since then, AOSs have widely been investigated and a-IGZO TFTs are now used in current flat-panel displays such as liquid-crystal displays (LCDs) in small-size smartphones, middle-size tablets and notebook computers, and 32” 4K LCDs as well as 77” 4K OLED TVs [10–13].

It is known for most TCOs, particularly, AOSs, *n*-type conduction is readily attained; while *p*-type conduction is relatively difficult because the VBM of oxides generally consists of localized oxygen *2p* orbitals due to the strong ionicity, for which the accepters have deep levels and the hole mobility is rather small. To expand the application of TCOs (including AOSs) for most semiconductor devices, the fabrication of *pn* junctions exclusively from semiconducting TCOs is essential. Therefore, much efforts have been devoted to exploring *p*-type semiconducting TCOs in the past two decades [14–17]. In 1997, Prof. Hosono group [14] proposed a chemical design concept for *p*-type TCOs, where its essence is to extend the VBM wave functions by introducing covalency in the metal–oxygen bonds, namely, the VBM consists of the resulting antibonding level and thus become dispersive. To avoid visible light absorption due to transitions in unfilled orbitals, metal cations are required to have a (pseudo-)closed shell (e.g., $(n-1)d^{10}ns^0$ and $(n-1)d^{10}ns^2$ electron configurations), and to form a dispersive VBM, their energy levels should be close

to those of the O 2*p* levels. There are a few examples of such appropriate cations; Cu⁺, Ag⁺ and Zn²⁺ for (n-1)*d*¹⁰*ns*⁰, and Sn²⁺, Pb²⁺ and Bi³⁺ for (n-1)*d*¹⁰*ns*². Among them, Cu⁺ has a 3*d* levels close to the O 2*p* levels and is widely chosen for *p*-type TCOs and other *p*-type semiconductors such as CuIn_xGa_{1-x}Se₂ (CIGS), an absorber material for solar cells [18]. In fact, Cu₂O is a naturally *p*-type oxide semiconductor with high hole mobilities of >70 cm²V⁻¹s⁻¹, and can produce *p*-channel TFTs exhibiting several cm²V⁻¹s⁻¹ of field-effect mobilities [19]. However, Cu₂O has a rather small band gap (2.17 eV) compared with those of TCOs (> 3.1 eV). Along with the above chemical design concept, Hosono et al [14] reported aluminate of Cu⁺, CuAlO₂ with the delafossite structure as a *p*-type TCO, which show considerable improvement over the first *p*-type TCO, NiO [20]. Since then, two families of Cu⁺-based TCOs, CuMO₂ (*M* = Al, Ga, In, Sc, etc.) [21–24] delafossites and non-delafossites including SrCu₂O₂ [25] and LaCuO*Ch* (*Ch* = chalcogen) [26–28], have been developed with the chemical design concept. It is known that Zn²⁺ has deeper 3*d* levels than those of Cu⁺, but shallower than Ga 3*d*, Cd 4*d* and In 4*d* levels and comparable to O 2*p* levels. As a result, Zn 3*d* as well as O 2*p* orbitals contribute to pushing up the VBM and to forming a dispersive VBM in ZnO [29]. It has been reported that ZnO can be converted to *p*-type by Li⁺ doping to the Zn²⁺ sites [30], N³⁻ doping to O²⁻ sites [31,32], etc., although there are still issues remaining on their stability and reproducibility. Sn²⁺ has occupied 4*s* orbitals slightly lower than O 2*p* orbitals and the VBM of SnO consists of hybridized orbitals of Sn 4*s* and O 2*p* and is spatially dispersive. SnO has a direct band gap of 2.7 eV and an indirect band gap of 0.7 eV, and exhibits naturally *p*-type conduction with drift and field-effect mobilities of several cm²V⁻¹s⁻¹ in thin films and TFTs [33,34].

Although many crystalline *p*-type TCOs have been developed with the above chemical design concept, it is difficult to achieve *p*-type conduction in amorphous ones, i.e.

AOSs. So far, amorphous $x\text{ZnO}\cdot\text{Rh}_2\text{O}_3$ ($x = 0.5\text{--}2.0$) [35,36], Cr_2O_3 [37] SnO_2 [38] have been reported to exhibit p -type conduction, but their hole mobilities are very small, $< 0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Further, there have been other compounds beyond oxides examined for high-mobility p -type amorphous semiconductors. For example, simple Cu-based simple chalcogenides ($\text{Cu}_{1.6}\text{S}$ and $\text{Cu}_{1.7}\text{Se}$) and chalcopyrites ($\text{Cu}M(\text{S},\text{Se})_2$, $M = \text{Al}, \text{Ga}, \text{and In}$) exhibit tunable p -type conductivities from 10^{-5} to 10^4 S cm^{-1} ; however, their TFTs didn't work because of the high-density subgap states [39]. Therefore, it is still a challenging issue to explore high-mobility p -type AOSs and beyond.

1.1.3 Doping Asymmetry in Inorganic Semiconductors

The controllability of carrier type, i.e., p -type (hole conducting) and n -type (electron conducting), is a fundamental and important requirement for a semiconductor to produce high-performance electronic devices with a homo pn junction structure. Currently, bipolar semiconduction is achieved in some semiconductors mainly by aliovalent substitutional doping. For example, silicon (4 valence electrons in a Si atom), which is the most common semiconductor used in integrated circuits, exhibits p -type and n -type conduction by doping B (3 valence electrons) and P (5 valence electrons), respectively [40]. However, bipolar semiconduction becomes more difficult for compound semiconductors, particularly, those with wide band gaps. ZnO is naturally n -type, but not p -type [41–45]. NiO is naturally doped p -type, but not n -type [20,42]. SnS is naturally a p -type semiconductor with a narrow band gap of 1.07 eV, but it is difficult to be doped n -type [46,47]. These doping asymmetry problems have hindered the potential applications of many such semiconductors with unique properties. In the last few decades, much effort has been made to understand the origin of the doping asymmetry particularly in wide-band gap

semiconductors and to overcome the doping asymmetry [43–45]. It is now known that *n*-type diamond and *p*-type ZnO can be achieved by choosing some dopants and designing some specific defect complexes.

Generally, the doping asymmetry is caused by three main reasons; (i) spontaneous formation of compensating defects, (ii) the desirable dopants have limited solubility, and (iii) the desirable dopants have sufficient solubility, but they produce deep levels, which are not ionized at working temperatures. The first reason is an intrinsic problem to the host material, which is the most difficult problem to be overcome. It is known that the formation energy of a charged defect depends linearly on the position of the Fermi level, E_F . When a semiconductor is doped *p*-type, E_F moves closer to the VBM. In the case, the formation energies of the charged acceptor defects increase and those of the compensating donor defects decrease. As a result, further *p*-type doping become more difficult. Conversely, a similar but opposite trend is found also for *n*-type doping. The second reason depends highly on the selected dopants and may be improved by fabrication condition (i.e. the chemical potentials of dopants and host elements, respectively). The third reason depends on the selected dopant (i.e. the ionic radius, electronegativity, etc.). Therefore, the latter two reasons can sometimes be solved by finding appropriate dopants and fabrication conditions.

First-principles density functional theory (DFT) has widely been used to calculate the formation energies and transition energies of intrinsic and extrinsic defects. Based on DFT calculations, various approaches have been proposed to overcome the doping asymmetry in semiconductors. Taking *p*-type doping of ZnO as an example, the following approaches has been suggested:

- (i) Solubility of acceptor impurities can be increased by adjusting their chemical

potential [48,49]. Raising the chemical potential of an acceptor dopant in the ZnO would increase the solubility of the dopant and suppress precipitate formation. For example, metastable NO and NO₂ can supply reactive nitrogen atoms more easily than N₂ can. Therefore, doping with NO and NO₂ should result in higher solubility of nitrogen compared to N₂ [49].

(ii) Ionization energy of an acceptor can be reduced by designing shallower dopants or dopant complexes [50–52]. For example, the ionization energy of N_O (N at an O site) can be reduced by replacing Zn with isovalent Mg or Be to form shallower N_{O+nMg_{Zn}} or N_{O+nBe_{Zn}} complexes. Therefore, Mg and Be could be good codopants pairs for nitrogen to achieve *p*-type ZnO [52].

(iii) Both ionization energy of an acceptor level and defect compensation can be reduced by modifying the host band structure near the band edge [43]. The valence band edge of ZnO can be modified by passivating codopants such as Ga and N. N combined with Ga creates a passivated defect band above the VBM. The shallow acceptor levels can be created by doping the passivated ZnO:(Ga+N) system with excessive N [43].

Despite many reports on *p*-type ZnO, there are still issues remaining on their stability and reproducibility, and no credible *p*-type ZnO has been reported to be suitable for practical light-emitting devices. Nevertheless, the above approaches would be also effective to solve the doping asymmetry problem in other materials. Further, more doping routes are desired to achieve stable and reproducible doping and carrier conversion.

1.2 Objectives of This Study

The final purpose of this work is to design both *n*-type and *p*-type doping in more variety of compound semiconductors. Specifically, this study have two objectives.

As reviewed in [Section 1.1.2](#), many *n*-type amorphous semiconductors represented by a-IGZO have been developed and have shown high electrons mobilities $> 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, several *p*-type amorphous semiconductors have been developed; however, they have not shown high hole mobilities comparable to the existing *n*-type amorphous semiconductors. Therefore, one objective of this study is to explore high-mobility *p*-type ionic amorphous semiconductors, for which the key is to design a highly-dispersed VBM. Ionic arsenides are expected to be potential candidates because the largely-spread *5p* orbitals of arsenic anion would shallow and high-dispersed VBM for a hole transport path even in an amorphous structure. In this study, amorphous BaZn_2As_2 was examined.

SnS is expected as an absorber material for solar cells, suffers from the doping asymmetry problem, as reviewed in [Section 1.1.3](#); that is, it is naturally doped *p*-type, but hardly *n*-type. However, *n*-type SnS is desired to construct *p*- SnS/n - SnS homojunctions for high performance solar cells. Despite much efforts for *n*-type doping in SnS , no realizable *n*-type SnS have been attained. On the other hand, Cs_2SnI_6 , a rarely studied perovskite variant, is gaining interest for photovoltaic applications due to its nontoxicity and chemical stability. Cs_2SnI_6 is naturally *n*-type doped and has not shown intrinsic *p*-type conduction. The other objective of this study is to clarify the origins of the doping asymmetry problem in these novel compound semiconductors including SnS and Cs_2SnI_6 and design effective counter doping routes for these semiconductors.

1.3 Outline of the Thesis

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 properties of a- BaZn_2As_2 were investigated. It was found

that the α -BaZn₂As₂ films exhibited band gaps of > 1.04 eV and p -type conduction with high hole mobilities ~ 10 cm² V⁻¹ s⁻¹. Further, growth of crystalline β -BaZn₂As₂ films and the fundamental properties of β -BaZn₂As₂ were also discussed.

In Chapter 3 “Chemical Origins of the Narrow Band Gap in β -BaZn₂As₂,” the electronic structure and chemical origins of the narrow band gap in β -BaZn₂As₂ 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 (H/DFT) calculations, and the ligand theory.

In Chapter 4 “Origins of Doping Asymmetry in SnS,” the defect physics of SnS was investigated by defect calculations based on DFT. Particularly, the origins of the doping asymmetry in SnS were discussed based on the DFT calculation results and the band alignment diagram. Further, aliovalent Sb³⁺ and Bi³⁺ doping in SnS was also theoretically assessed and found not effective for n -type doping.

In Chapter 5 “ n -Type Conversion of SnS by Geometrical Doping Route,” n -type conduction was attained in isovalently Pb-substituted SnS films. The Pb substitution reduced the VBM and CBM, and thus reduced the severity of the doping asymmetry. More importantly, DFT calculations suggest that the substitution invoked a geometrical size effect that enlarges the interlayer distance and subsequently induces the formation of Sn and Pb cation interstitials, which result in the electron doping.

In Chapter 6 “Electronic Structure of a Perovskite Variant Cs₂SnI₆,” the electronic structure of a recently-reported perovskite variant Cs₂SnI₆ was studied by HDFT calculations. The real oxidation state of Sn in Cs₂SnI₆ was revealed closer to +2 similar to that in CsSnI₃, rather than +4 expected from a simple ionic model of Cs⁺₂Sn⁴⁺I⁻₆. The chemical stability and origin of the band gap were discussed by bonding nature analysis.

In [Chapter 7](#) “Intrinsic Defects in a Perovskite Variant Cs_2SnI_6 ,” HDFT calculations were performed to investigate the properties of intrinsic defects and the doping mechanism in Cs_2SnI_6 . Iodine vacancy and tin interstitial were found to be the dominant defects for the intrinsic n -type conduction in Cs_2SnI_6 . It was found that p -type conduction is difficult in Cs_2SnI_6 because of its too shallow VBM (i.e. too large IP). The origin of the high shallow VBM was also discussed by chemical bonding analysis in comparison with other related compounds.

In [Chapter 8](#) “General Conclusions”, this study is summarized and future perspective is described.

References

- [1] K. L. Chopra, S. Major, and D. K. Pandya, *Thin Solid Films* **102**, 1 (1983).
- [2] T. Minami, *Thin Solid Films* **516**, 5822 (2008).
- [3] H. Kim, C. M. Gilmore, A. Piqu , J. S. Horwitz, H. Mattoussi, H. Murata, Z. H. Kafafi, and D. B. Chrisey, *J. Appl. Phys.* **86**, 6451 (1999).
- [4] I. Hamberg and C. G. Granqvist, *J. Appl. Phys.* **60**, R123 (1986).
- [5] H. Nakazawa, Y. Ito, E. Matsumoto, K. Adachi, N. Aoki, and Y. Ochiai, *J. Appl. Phys.* **100**, 093706 (2006).
- [6] H. Hosono, N. Kikuchi, N. Ueda, and H. Kawazoe, *J. Non. Cryst. Solids* **198–200**, 165 (1996).
- [7] S. Narushima, M. Orita, M. Hirano, and H. Hosono, *Phys. Rev. B* **66**, 035203 (2002).
- [8] K. Nomura, A. Takagi, T. Kamiya, H. Ohta, M. Hirano, and H. Hosono, *Nature* **432**, 488 (2004).
- [9] W. E. Spear and P. G. LeComber, *Solid State Commun.* **17**, 1193 (1975).

- [10] T. Kamiya, K. Nomura, and H. Hosono, *J. Disp. Technol.* **5**, 273 (2009).
- [11] T. Kamiya and H. Hosono, *NPG Asia Mater.* **2**, 15 (2010).
- [12] T. Kamiya, K. Nomura, and H. Hosono, *Sci. Technol. Adv. Mater.* **11**, 044305 (2010).
- [13] J. S. Park, W. J. Maeng, H. S. Kim, and J. S. Park, *Thin Solid Films* **520**, 1679 (2012).
- [14] H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, and H. Hosono, *Nature* **389**, 939 (1997).
- [15] H. Kawazoe, H. Yanagi, K. Ueda, and H. Hosono, *MRS Bull.* **25**, 28 (2000).
- [16] H. Yanagi, H. Kawazoe, A. Kudo, M. Yasukawa, and H. Hosono, *J. Electroceramics* **4**, 407 (2000).
- [17] A. N. Banerjee and K. K. Chattopadhyay, *Prog. Cryst. Growth Charact. Mater.* **50**, 52 (2005).
- [18] P. Reinhard, A. Chirila, P. Blosch, F. Pianezzi, S. Nishiwaki, S. Buecheler, and A.N. Tiwari, *IEEE J. Photovoltaics* **3**, 572 (2013).
- [19] B. K. Meyer, A. Polity, D. Reppin, M. Becker, P. Hering, P. J. Klar, T. Sander, C. Reindl, J. Benz, M. Eickhoff, C. Heiliger, M. Heinemann, J. Bläsing, A. Krost, S. Shokovets, C. Müller, and C. Ronning, *Phys. Status Solidi B* **249**, 1487 (2012).
- [20] H. Sato, T. Minami, S. Takata, and T. Yamada, *Thin Solid Films* **236**, 27 (1993).
- [21] H. Yanagi, S. Inoue, K. Ueda, H. Kawazoe, H. Hosono, and N. Hamada, *J. Appl. Phys.* **88**, 4159 (2000).
- [22] K. Ueda, T. Hase, H. Yanagi, H. Kawazoe, H. Hosono, H. Ohta, M. Orita, and M. Hirano, *J. Appl. Phys.* **89**, 1790 (2001).
- [23] H. Yanagi, T. Hase, S. Ibuki, K. Ueda, and H. Hosono, *Appl. Phys. Lett.* **78**, 1583 (2001).
- [24] N. Duan, A. W. Sleight, M. K. Jayaraj, and J. Tate, *J. Appl. Phys.* **77**, 1325 (2000).

- [25] A. Kudo, H. Yanagi, H. Hosono, and H. Kawazoe, *Appl. Phys. Lett.* **73**, 220 (1998).
- [26] K. Ueda, S. Inoue, S. Hirose, H. Kawazoe, and H. Hosono, *Appl. Phys. Lett.* **77**, 2701 (2000).
- [27] H. Hiramatsu, K. Ueda, H. Ohta, M. Orita, M. Hirano, and H. Hosono, *Appl. Phys. Lett.* **81**, 598 (2002).
- [28] T. Kamiya, K. Ueda, H. Hiramatsu, H. Kamioka, H. Ohta, M. Hirano, and H. Hosono, *Thin Solid Films* **486**, 98 (2005).
- [29] P. Schröer, P. Krüger, and J. Pollmann, *Phys. Rev. B* **47**, 6971 (1993).
- [30] J. Lee, S. Cha, J. Kim, H. Nam, S. Lee, W. Ko, K.L. Wang, J. Park, and J. Hong, *Adv. Mater.* **23**, 4183 (2011).
- [31] M. Joseph, H. Tabata, and T. Kawai, *Jpn. J. Appl. Phys.* **38**, L1205 (1999).
- [32] A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, and M. Kawasaki, *Nat. Mater.* **4**, 42 (2005).
- [33] Y. Ogo, H. Hiramatsu, K. Nomura, H. Yanagi, T. Kamiya, M. Hirano, and H. Hosono, *Appl. Phys. Lett.* **93**, 032113 (2008).
- [34] Y. Ogo, H. Hiramatsu, K. Nomura, H. Yanagi, T. Kamiya, M. Kimura, M. Hirano, and H. Hosono, *Phys. Status Solidi A* **206**, 2187 (2009).
- [35] S. Narushima, H. Mizoguchi, K. Shimizu, K. Ueda, H. Ohta, M. Hirano, T. Kamiya, and H. Hosono, *Adv. Mater.* **15**, 1409 (2003).
- [36] T. Kamiya, S. Narushima, H. Mizoguchi, K. Shimizu, K. Ueda, H. Ohta, M. Hirano, and H. Hosono, *Adv. Funct. Mater.* **15**, 968 (2005).
- [37] P. Qin, G. Fang, N. Sun, X. Fan, Q. Zheng, F. Chen, J. Wan, and X. Zhao, *Thin Solid Films* **519**, 4334 (2011).

- [38] C.-W. Ou, Z. Y. Ho, Y.-C. Chuang, S.-S. Cheng, M.-C. Wu, K.-C. Ho, and C.-W. Chu, *Appl. Phys. Lett.* **92**, 122113 (2008).
- [39] H. Hiramatsu, H. Yanagi, T. Kamiya, M. Hirano, N. Matsunami, K. Shimizu, and H. Hosono, *Phys. Status Solidi A* **205**, 2007 (2008).
- [40] D. A. Neamen, *Semiconductor Physics and Devices: Basic Principles*, 3rd Ed. (McGraw-Hill, New York, 2003), pp. 115–117.
- [41] S. B. Zhang, S.-H. Wei, and A. Zunger, *Phys. Rev. B* **63**, 075205 (2001).
- [42] S. Lany, J. Osorio-Guillén, and A. Zunger, *Phys. Rev. B* **75**, 241203 (2007).
- [43] Y. Yan, J. Li, S.-H. Wei, and M. M. Al-Jaassim, *Phys. Rev. Lett.* **98**, 135506 (2007).
- [44] Y. Yan and S.-H. Wei, *Phys. Status Solidi B* **245**, 641 (2008).
- [45] V. Avrutin, D. J. Silversmith, and H. Morkoç, *Proc. IEEE* **98**, 1269 (2010).
- [46] F.-Y. Ran, Z. Xiao, H. Hiramatsu, H. Hosono, and T. Kamiya, *Appl. Phys. Lett.* **104**, 072106 (2014).
- [47] P. Sinsersuksakul, R. Chakraborty, S. B. Kim, S. M. Heald, T. Buonassisi, and R. G. Gordon, *Chem. Mater.* **24**, 4556 (2012).
- [48] Y. Yan, S. B. Zhang, S. J. Pennycook, and S. T. Pantelides, *Mater. Res. Soc. Symp. Proc.* **666**, F2.6 (2001).
- [49] Y. Yan, S. B. Zhang, and S. T. Pantelides, *Phys. Rev. Lett.* **86**, 5723 (2001).
- [50] Y. R. Ryu, T. S. Lee, and H. M. White, *Appl. Phys. Lett.* **83**, 87 (2003).
- [51] S. Limpijumnong, S. B. Zhang, S.-H. Wei, and C. H. Park, *Phys. Rev. Lett.* **92**, 155504 (2004).
- [52] J. Li, S.-H. Wei, S.-S. Li, and J.-B. Xia, *Phys. Rev. B* **74**, 081201R (2006).

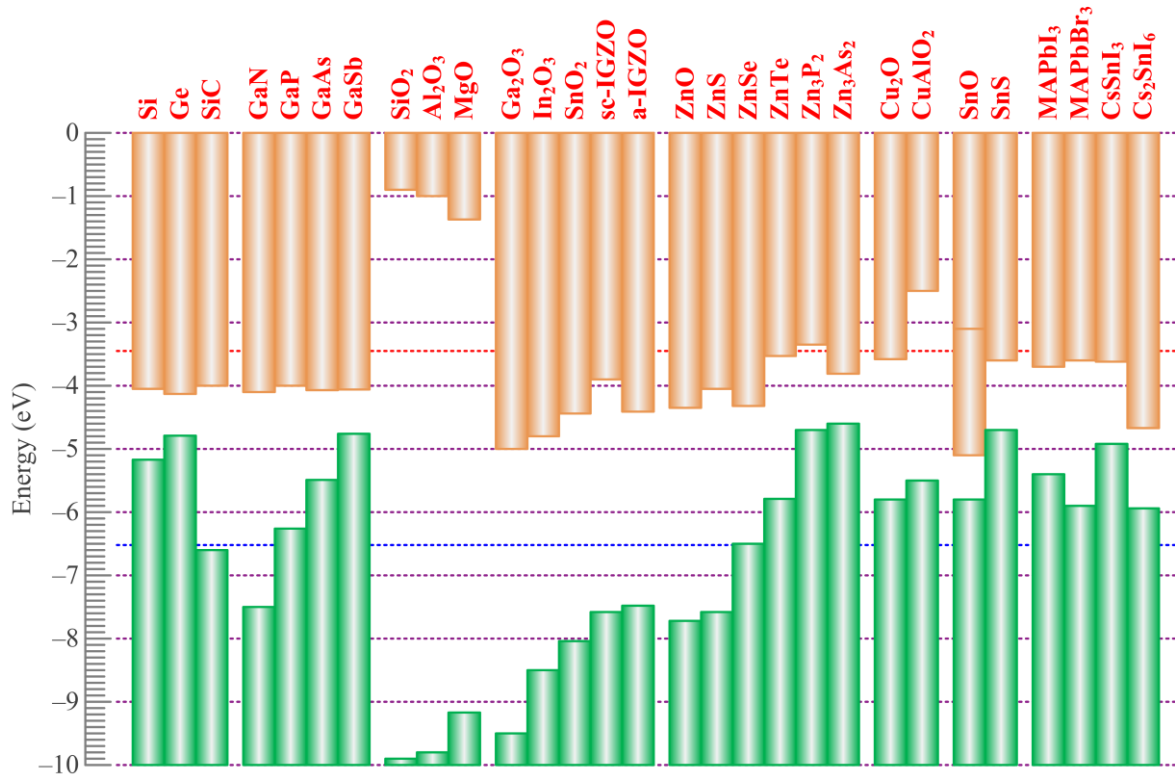


Figure 1.1. Band alignment based on the ionization potential (*IP*) and electron affinity (*EA*) from literatures.

Chapter 2

High-Mobility *p*-Type Amorphous Semiconductor BaZn₂As₂

2.1 Introduction

Amorphous semiconductors such as hydrogenated amorphous silicon (a-Si:H) have advantages over crystalline ones from the viewpoint of processing, e.g., low-temperature deposition and large-area uniformity, which enables developing large-area electronic devices such as solar cells and thin-films transistors (TFTs) for flat-panel displays [1]. In the last decade, *n*-type amorphous oxide semiconductors (AOSs) represented by amorphous In–Ga–Zn–O (a-IGZO) have widely been investigated and are now commercialized owing to their advantages such as high electron mobilities $> 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [2–5] over the conventional amorphous semiconductors such as a-Si:H. On the other hand, *p*-type AOSs with high hole mobilities are important and are desired to make high-performance all-AOS electronic devices based on CMOS circuits. Although some *p*-type AOSs such as amorphous $x\text{ZnO}\cdot\text{Rh}_2\text{O}_3$ ($x = 0.5\text{--}2.0$) [6,7], Cr_2O_3 [8], and SnO_2 [9] have been reported, their hole mobilities are very small, $< 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

It is known that the valence band maximum (VBM) of most oxide semiconductors consists mainly of fully occupied $2p$ orbitals of oxygen anions with a large electronegativity. Hence the dispersion of VBM is small (i.e. the hole effective mass is large and the hole mobility is small) and the ionization potential (IP) is large (i.e. the hole

is energetically unstable), causing the *p*-type doping difficulty for oxide semiconductor, particularly, in an amorphous phase.

On the other hand, effective *p*-type doping and relatively high hole mobility have been attained in crystalline Cu₂O and SnO, because the occupied 3*d* orbitals of Cu⁺ cation and the occupied Sn 5*s* orbitals of Sn²⁺ cation hybridize with 2*p* orbitals of oxygen anion, leading to the shallower and more dispersive VBMs in Cu₂O and SnO than other typical oxide semiconductors. Currently, crystalline Cu₂O and SnO can produce *p*-type channel TFTs exhibiting several cm² V⁻¹ s⁻¹ of field-effect mobilities [10–12]. Amorphous SnO *p*-channel TFTs have been also reported, but their TFT mobilities were only ~0.01 cm² V⁻¹ s⁻¹ [13]. Therefore, the exploration of high-mobility *p*-type amorphous semiconductors is still of extreme significance for developing large-area electronic devices.

To explore high-mobility *p*-type amorphous semiconductors, the following properties would be essential to select potential candidate compounds; (i) the VBM is shallow enough so that *p*-type doping can readily attained, (ii) the VBM is dispersive so that the hole mobility can be high, and (iii) the compound is mainly ionic so that the hole transport passes can be retained in the amorphous structure [14,15]. It is considered that ionic metal pnictides such as Zn₃P₂ and Zn₃As₂, the VBMs of which consist mainly of largely-spread *p* orbitals of pnictogen anions, should satisfy the above requirements (see Fig. 1.1) and would have the potential for high-mobility *p*-type amorphous semiconductors. Here, ternary pnictide BaZn₂As₂ rather than binary Zn₃As₂ is finally selected as a candidate compound, because it would be easier for the former one to form a stable amorphous structure due to its higher melting/crystallization temperatures [16,17]. Further, BaZn₂As₂ crystallizes into two phases, i.e., orthorhombic α-BaZn₂As₂ (space group *Pnma*) [16] and tetragonal β-BaZn₂As₂ (space group *I4/mmm*) [17] as shown in the right of Fig. 2.1. The

β -BaZn₂As₂ phase is isostructural to the “122” iron-based superconductors such as (Ba,K)Fe₂As₂ [18,19] and would be interested for developing new electronic functions; e.g., Zhao *et al.* [20] have synthesized polycrystalline (Ba,K)(Zn,Mn)₂As₂ for diluted magnetic semiconductors.

In this chapter, amorphous BaZn₂As₂ (a-BaZn₂As₂) thin films were fabricated by pulsed laser deposition (PLD). The structural, optical, and electrical properties of a-BaZn₂As₂ were investigated. The a-BaZn₂As₂ films exhibited band gaps of > 1.04 eV and p-type conduction with high hole mobilities from 1 to ~10 cm² V⁻¹ s⁻¹. Further, the crystallization of a-BaZn₂As₂ and the fundamental properties of crystallized β -BaZn₂As₂ were also discussed.

2.2 Experimental and Computational Details

2.2.1 Target Fabrication

Thin films were grown by PLD. The BaZn₂As₂ PLD targets were synthesized through a solid-state reaction from elementary Ba, Zn and As. Ba pieces, fresh Zn powders, and As powders, which were mixed at the stoichiometric ratio, sealed in an evacuated quartz tube, and heated at 700 °C for 20 hours. The obtained reaction product was ground, pressed into pellets (8 mm in diameter), and further pressed with a cold isostatic press (CIP) apparatus at 250 MPa. Then, the pellets were sealed in evacuated quartz tubes and annealed at 700 °C for 20 hours, and then furnace-cooled to room temperature (RT) to obtain α -BaZn₂As₂. To obtain β -BaZn₂As₂ phase, the pellets were annealed at a higher temperature of 1000 °C and rapidly quenched by being dropped into water to stabilize the metastable β -BaZn₂As₂ phase. All the target fabrication processes except for the CIP, the sealing and the heating were conducted in an argon-filled glove box. Besides, to obtain stoichiometric amorphous

BaZn₂As₂ thin films, a composition-optimized Zn-rich target (nominal atomic ratio is Ba: Zn: As = 1: 4.0: 2.5) was needed and fabricated by almost the same way except for a lower annealing temperature for the pellet (500 °C) to avoid Zn precipitation.

2.2.2 Thin Film Growth

~100 nm-thick amorphous BaZn₂As₂ (a-BaZn₂As₂) thin films were deposited on silica glass substrates at room temperature (RT) by PLD using a KrF excimer laser ($\lambda = 248$ nm; pulse duration = 20 ns; repetition frequency = 10 Hz). A composition-optimized Zn-rich target (the nominal atomic ratio of Ba: Zn: As = 1.0: 4.0: 2.5) was used to obtain nearly stoichiometric amorphous BaZn₂As₂ thin films. The as-deposited a-BaZn₂As₂ films were confirmed to be insulating and post-annealing was conducted to obtain electrical conductivity. For this, the a-BaZn₂As₂ films were annealed at $T_{\text{ann}} = 300\text{--}500$ °C for 1 h in evacuated silica-glass ampules, where a small amount of Zn₃As₂ powder was contained to suppress the evaporation of Zn and As elements during the annealing process.

Additionally, epitaxial β -BaZn₂As₂ thin films were also grown by the reactive solid-phase epitaxy (R-SPE) method [21,22]. Firstly, a metallic Zn layer (~ 5 nm in thickness) was deposited on a single-crystal MgO (001) at RT by PLD, followed by deposition of an a-BaZn₂As₂ layer at RT in the same PLD chamber. Next, the a-BaZn₂As₂ / Zn / MgO sample was covered by an MgO (001) plate and annealed at 900 °C for 30 minutes in an argon-filled stainless steel tube, where a small amount of Zn₃As₂ powders was contained to suppress the evaporation of the Zn and As elements during annealing.

2.2.3 Characterization

X-ray diffraction (XRD) patterns of the bulk samples were measured with a conventional powder XRD instrument (RINT2500, Rigaku). The temperature (T)

dependence of dc electrical conductivity (σ) of the β -BaZn₂As₂ sample was measured by the conventional four-probe method with a physical property measure measurement system (PPMS, Quantum Design) up to 400 K.

Crystalline quality and orientation of the grown films were examined with a high-resolution XRD (HR-XRD) instrument (Smart Lab, Rigaku). Out-of-plane ($2\theta/\omega$ synchronous scan) and in-plane ($2\theta/\chi/\phi$ synchronous scan) XRD patterns were measured to determine epitaxial relationships between the films and the MgO substrates and to calculate lattice parameters. Chemical compositions were determined by X-ray fluorescence (ZSX-100e, Rigaku) with a polycrystalline sample as a reference. Optical absorption spectra from ultraviolet to near-infrared region were recorded in air using a conventional spectrophotometer (U4100, Hitachi), and those in the mid-infrared region were performed in vacuum with a Fourier transform infrared (FTIR) spectrometer (Vertex 70v, Bruker).

2.3 Results and Discussion

2.3.1 Structural Properties of Amorphous BaZn₂As₂ Films

The XRD patterns of BaZn₂As₂ bulk samples are shown in the bottom of Fig. 2.1. The one synthesized at 700 °C crystallized into the orthorhombic α -BaZn₂As₂ phase; while the one synthesized at 1000 °C crystallized into the β -BaZn₂As₂ phase, which had been stabilized by the water quenching process. These results are consistent with the literatures [16,17]. The XRD patterns of the BaZn₂As₂ films are shown in the top of Fig. 2.1. The pattern of the as-deposited film showed no sharp diffraction peak attributable to the crystalline α - and β -BaZn₂As₂ phases. The halo peak around $\sim 21^\circ$ is assigned to the silica glass substrate. These features indicate that the as-deposited film was amorphous. The films annealed at

300 and 400 °C kept the amorphous phase since their XRD patterns are unchanged as that of the as-deposited one. For the film annealed at 500 °C, the XRD pattern has an extra wide halo peak around ~35° and three weak diffraction peaks at 16.2°, 26.1° and 26.2°. Although the former cannot be attributed to the crystalline structure, the later three are the α -BaZn₂As₂ 002, α -BaZn₂As₂ 103 and β -BaZn₂As₂ 004 diffraction peaks, respectively, indicating that crystallization into polymorphic α - and β -BaZn₂As₂ initiated in the a-BaZn₂As₂ film by the 500 °C annealing. Table 1 shows the chemical composition of two typical film samples. Both the films had nearly stoichiometric compositions, which were not changed significantly during the annealing process.

2.3.2 Optical Properties of Amorphous BaZn₂As₂ Films

Figure 2.2a shows optical absorption spectra. The absorption coefficients level off in the high energy region at > 3.0 eV independent of T_{ann} . Figure 2.2b shows the $(\alpha hv)^{1/2} - hv$ plots (Tauc's plots) to evaluate optical bandgaps of the a-BaZn₂As₂ films. The as-deposited a-BaZn₂As₂ exhibits a distinct linear region in the Tauc's plot. Extrapolating this linear region to the abscissa yields the Tauc's bandgap of 1.04 eV, which is close to those of simple zinc arsenides (e.g., 0.99 eV for Zn₃As₂ [23] and 0.98 eV for ZnAs₂ [24]). For the annealed films, the absorption spectra slightly shifted toward higher energies. The bandgaps of the films annealed at 300, 400 and 500 °C were 1.24, 1.32 and 1.35 eV, respectively (i.e., the post-annealing increased the bandgap by 0.20–0.31 eV). These results indicate that the band gap are tunable with T_{ann} , the reason for which has not been revealed, but would be attributed to structural relaxation in the annealing process.

2.3.3 Electrical Properties of Amorphous BaZn₂As₂ Films

The as-deposited a-BaZn₂As₂ films were highly resistive. To achieve electrical conduction

in a-BaZn₂As₂ films, post-annealing was performed. Figure 2.3 shows the electrical properties of the annealed a-BaZn₂As₂ films. All the annealed films exhibited *p*-type conduction. Figure 2.3a plots the hole mobilities (μ_h) as a function of T_{ann} , which exhibits an increasing trend with T_{ann} . At $T_{\text{ann}} = 300$ °C, μ_h of 0.6–1.6 cm² V⁻¹ s⁻¹ were obtained. For higher $T_{\text{ann}} = 400$ °C, μ_h was increased to 1.8–9.8 cm² V⁻¹ s⁻¹, which were comparable with those of *n*-type AOSs [5]. At $T_{\text{ann}} = 500$ °C, μ_h further increased to 20.2 cm² V⁻¹ s⁻¹, which would be attributed partly to the existence of the crystallized β -BaZn₂As₂ phase. The hole densities (p) and conductivities (σ) were at the orders of 10¹⁸–10¹⁹ cm⁻³ and 1–20 S cm⁻¹, as shown in Fig. 2.3b and 2.3c, respectively. No clear T_{ann} dependences were observed for p and σ . Figure 2.3d plots μ_h as a function of p , exhibiting a decreasing trend. There would be two major mechanisms that affect the hole mobility. That is, Fig. 2.3a suggests that film quality would be improved by higher T_{ann} annealing, and Fig. 2.3d implies that carrier scattering due to ionized acceptors deteriorates μ_h at higher p [25], and provides an expectation that further reduction of p will achieve higher μ_h .

2.3.4 Epitaxial Growth and Narrow Band Gap of Crystalline β -BaZn₂As₂

The HR-XRD patterns of the BaZn₂As₂ thin film annealed at 900 °C are shown in Fig. 2.4a. In the out-of-plane XRD pattern (the top panel of Fig. 2.4a), only intensive β -BaZn₂As₂ 00 l along with MgO 001 diffraction peaks were observed. In the in-plane HR-XRD pattern (the bottom panel of Fig. 2.4a), only BaZn₂As₂ 200 and 400 diffraction peaks together with MgO 200 and 400 diffraction peaks were observed. These results indicate epitaxial β -BaZn₂As₂ thin films were obtained by the R-SPE process with the epitaxial relationship of out-of-plane BaZn₂As₂ (00 l) // MgO (001) and in-plane BaZn₂As₂ (200) // MgO (200). Note that no diffraction peak of metallic Zn was observed, indicating the ultrathin Zn layer should have been sacrificed in the R-SPE process and played as an epitaxy initializer,

similar to the roles of epitaxial Cu and ZnO layers for epitaxial growth of LaCuOS [21] and InGaO₃(ZnO)_m [22], respectively.

The optical absorption spectrum of the epitaxial β -BaZn₂As₂ film measured by a conventional spectrophotometer is shown in Fig. 2.3b. An absorption edge was observed at <1.0 eV; but the absorption coefficient (α) didn't vanish to zero or reach a minimum until 0.5 eV, suggesting the band gap should be less than 0.5 eV. To evaluate such small band gap for β -BaZn₂As₂, FTIR spectra were further measured in the lower energy region from 0.04 eV to 0.93 eV as shown in Fig. 2.4c. A strong absorption peak is observed in 0.05–0.20 eV for the film / substrate sample. This peak is caused by MgO substrate (the blue dashed lines in Fig. 2.4c), which hinders the band gap determination more or less. By subtracting the absorption spectrum of the MgO substrate ($\alpha_{\text{substrate}}$), the net absorption of the film ($\alpha_{\text{film}} - \alpha_{\text{substrate}}$) is plotted by the red dashed line, showing that an absorption edge would be at 0.23 eV. The band gap was further examined from the intrinsic region of electrical conductivity (σ) of a polycrystalline β -BaZn₂As₂ sample. The σ (in logarithmic coordinate) vs. $1/T$ Arrhenius plot shown in Fig. 2.4d exhibits two linear regions between 10 and 50 K and between 190 and 310 K, respectively. The high- T linear region should be attributed to the intrinsic region of σ and can be expressed by $\sigma = \sigma_0 \exp(-E_a/k_B T)$, where σ_0 is the pre-exponential constant, k_B is the Boltzmann constant, and E_a is the activation energy. The low- T linear region could be attributed, for example, to the variable range hopping (VRH) model, the saturation regime of the ionization of donors, and very shallow donors. For example, the σ - T data were fitted by a combined expression $\sigma(T) = \sigma_0 \exp(-E_a/k_B T) + \sigma_{\text{vrh}} \exp[-(T_0/T)^{1/4}]$, where the latter express the VRH model with constants σ_{vrh} and T_0 [26], as drawn by the red curve. The fit gave intrinsic E_a value of 0.114 eV and thus the band gap is $E_g = 2E_a = 0.23$ eV.

2.4 Conclusions

The a-BaZn₂As₂ thin films were grown by PLD. The optical band gap of a-BaZn₂As₂ was determined to be 1.04 eV in the as-deposited state, and increased up to 1.37 eV with increasing the annealing temperature to 500 °C. The annealed films exhibited p-type conductivities with hole mobilities up to ~10 cm²V⁻¹s⁻¹ by keeping amorphous structures, and partially-crystallized films exhibited higher hole mobilities ~20 cm²V⁻¹s⁻¹. This achievement indicates that high hole mobilities would be attained even in amorphous semiconductors if heavy anions are employed. Crystallization was observed in the a-BaZn₂As₂ films annealed at $T_{\text{ann}} \geq 500$ °C and epitaxial growth of β -BaZn₂As₂ films was achieved by the R-SPE method. The band gap of β -BaZn₂As₂ was estimated to be 0.23 eV, unexpectedly much smaller even than a-BaZn₂As₂.

References

- [1] R. A. Street, *Hydrogenated amorphous silicon*, Cambridge University Press, Cambridge (1991).
- [2] E. Fortunato, P. Barquinha, A. Pimentel, A. Gonçalves, A. Marques, R. Martins, and L. Pereira, *Appl. Phys. Lett.* **85**, 2541 (2004).
- [3] K. Nomura, H. Ohta, K. Ueda, T. Kamiya, M. Hirano, and H. Hosono, *Science* **300**, 1269 (2003).
- [4] K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, and H. Hosono, *Nature* **432**, 488 (2004).
- [5] T. Kamiya, K. Nomura, and H. Hosono, *Sci. Technol. Adv. Mater.* **11**, 044305 (2010).
- [6] S. Narushima, H. Mizoguchi, K. Shimizu, K. Ueda, H. Ohta, M. Hirano, T. Kamiya, and H. Hosono, *Adv. Mater.* **15**, 1409 (2003).

- [7] T. Kamiya, S. Narushima, H. Mizoguchi, K. Shimizu, K. Ueda, H. Ohta, M. Hirano, and H. Hosono, *Adv. Funct. Mater.* **15**, 968 (2005).
- [8] P. Qin, G. Fang, N. Sun, X. Fan, Q. Zheng, F. Chen, J. Wan, and X. Zhao, *Thin Solid Films* **519**, 4334 (2011).
- [9] C.-W. Ou, Z. Y. Ho, Y.-C. Chuang, S.-S. Cheng, M.-C. Wu, K.-C. Ho, and C.-W. Chu, *Appl. Phys. Lett.* **92**, 122113 (2008).
- [10] Y. Ogo, H. Hiramatsu, K. Nomura, H. Yanagi, T. Kamiya, M. Hirano, and H. Hosono, *Appl. Phys. Lett.* **93**, 032113 (2008).
- [11] M. Liao, Z. Xiao, F.-Y. Ran, H. Kumomi, T. Kamiya, and H. Hosono, *ECS J. Solid State Sci. Technol.* **4**, Q26 (2015).
- [12] K. Matsuzaki, K. Nomura, H. Yanagi, T. Kamiya, M. Hirano, and H. Hosono, *Appl. Phys. Lett.* **93**, 202107 (2008).
- [13] C.-W. Ou, Dhananjay, Z. Y. Ho, Y.-C. Chuang, S.-S. Cheng, M.-C. Wu, K.-C. Ho, and C.-W. Chu, *Appl. Phys. Lett.* **92**, 122113 (2008).
- [14] H. Hosono, N. Kikuchi, N. Ueda, and H. Kawazoe, *J. Non. Cryst. Solids* **198-200**, 165 (1996).
- [15] H. Hosono, *J. Non. Cryst. Solids* **352**, 851 (2006).
- [16] P. Klüfers, A. Mewis, *Z. Naturforsch.* **33b**, 151 (1978).
- [17] A. Hellmann, A. Löhken, A. Wurth, A. Mewis, *Z. Naturforsch.* **62b**, 155 (2007).
- [18] M. Rotter, M. Tegel, and D. Johrendt, *Phys. Rev. Lett.* **101**, 107006 (2008).
- [19] T. Katase, H. Hiramatsu, H. Yanagi, T. Kamiya, M. Hirano, and H. Hosono, *Solid State Commun.* **149**, 2121 (2009).
- [20] K. Zhao, Z. Deng, X.C. Wang, W. Han, J.L. Zhu, X. Li, Q.Q. Liu, R.C. Yu, T. Goko, B. Frandsen, L. Liu, F.L. Ning, Y.J. Uemura, H. Dabkowska, G.M. Luke, H. Luetkens,

- E. Morenzoni, S.R. Dunsiger, A. Senyshyn, P. Böni, C.Q. Jin, Nat. Commun. **4**, 1442 (2013).
- [21] H. Hiramatsu, K. Ueda, H. Ohta, M. Orita, M. Hirano, and H. Hosono, Appl. Phys. Lett. **81**, 598 (2002).
- [22] H. Ohta, K. Nomura, M. Orita, M. Hirano, K. Ueda, T. Suzuki, Y. Ikuhara, and H. Hosono, Adv. Funct. Mater. **13**, 139 (2003).
- [23] J. Misiewicz and J. M. Pawlikowski, Solid State Commun. **32**, 687 (1979).
- [24] A. V. Mudryi, A. I. Patuk, I. A. Shakin, A. E. Kalmykov, S. F. Marenkin, and A. M. Raukhan, Mater. Chem. Phys. **44**, 151 (1996).
- [25] D. A. Neamen, *Semiconductor Physics and Devices: Basic Principles*, 3rd Ed. (McGraw-Hill, New York, 2003), pp. 115–117.
- [26] N. F. Mott, Philos. Mag. **19**, 835 (1969).

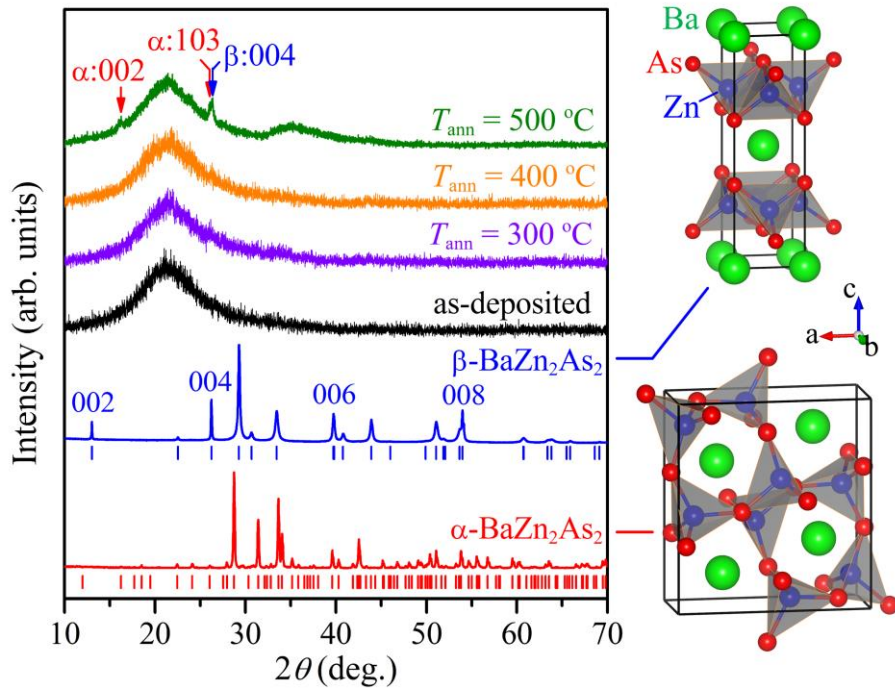


Figure 2.1. XRD patterns of BaZn₂As₂ films deposited at room temperature and annealed at various temperature (T_{ann}) along with those of polycrystalline α - and β -BaZn₂As₂ bulks for comparison. The crystal structures of α -BaZn₂As₂ (α -BaCu₂S₂-type, space group $Pnma$) and β -BaZn₂As₂ (ThCr₂Si₂-type, space group $I4/mmm$) are also shown on the right.

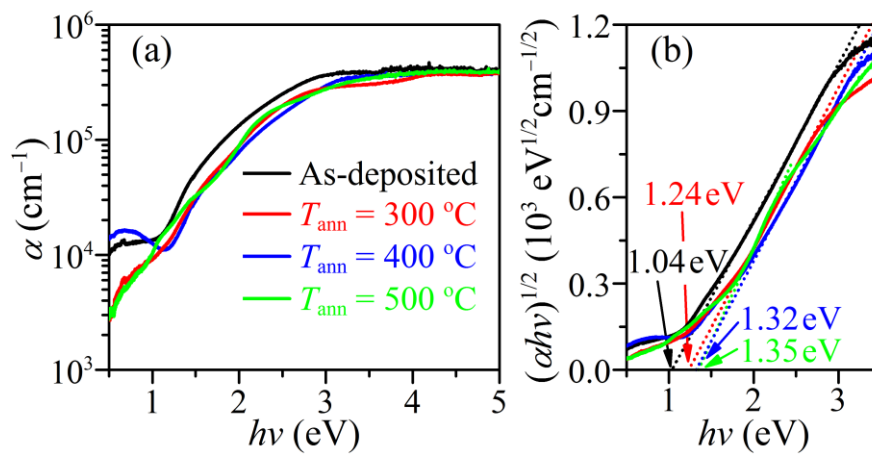


Figure 2.2. Optical properties of amorphous BaZn₂As₂. (a) Optical absorption spectra and (b) $(\alpha h\nu)^{1/2} - h\nu$ plots of as-deposited and annealed films. The obtained optical bandgaps are given in (b).

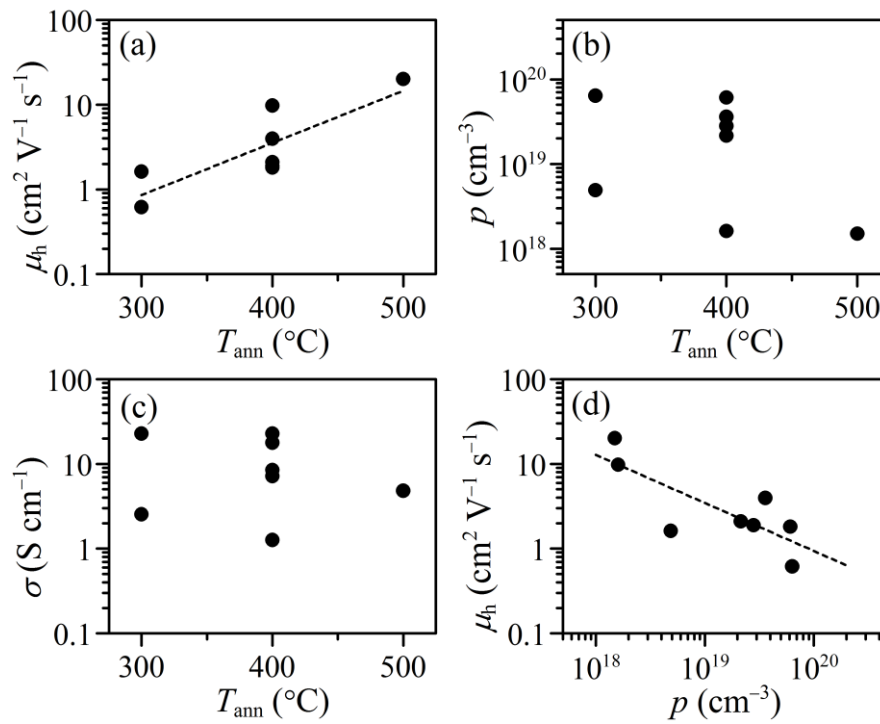


Figure 2.3. Electrical properties of amorphous BaZn₂As₂. (a) Hole mobility (μ_h), (b) hole density (p), and (c) conductivity (σ) of amorphous BaZn₂As₂ films annealed at various temperatures (T_{ann}). (d) μ_h plotted as a function of p .

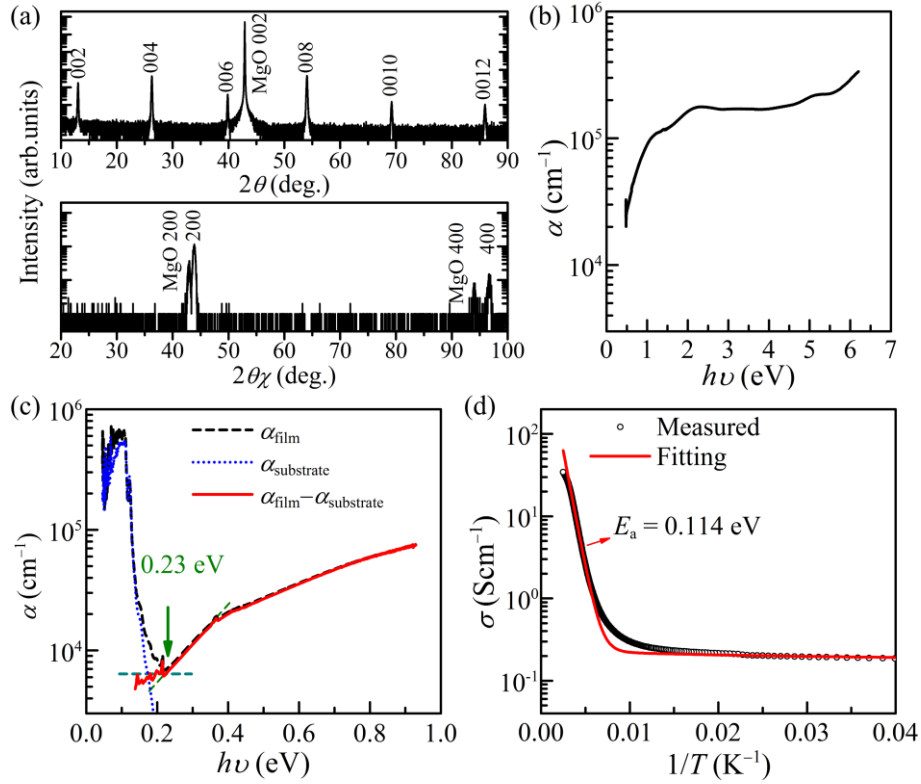


Figure 2.4. (a) Out-of-plane and in-plane HR-XRD pattern of BaZn₂As₂ thin film after annealing at 900 °C. (b and c) Optical spectra of epitaxial β -BaZn₂As₂ film (b) in near-infrared–ultraviolet region and (c) in mid infrared region. (d) T dependence of σ for polycrystalline β -BaZn₂As₂ sample. The red curve is a fit to $\sigma(T) = \sigma_0 \exp(-E_a/k_B T) + \sigma_{\text{vrh}} \exp[-(T_0/T)^{1/4}]$.

Chapter 3

Chemical Origins of the Narrow Band Gap in β -BaZn₂As₂

3.1 Introduction

Layered mixed-anion compounds including LaCuChO ($Ch = S, Se, Te$) [1–2], LaT_MP_nO ($T_M = Mn, Zn; P_n = P, As$) [3–5] and LaT_{M'}P_nO ($T_{M'} = Fe, Ni; P_n = P, As$) [6–8] exhibit a wide variety of electronic phenomena such as wide gap p -type semiconduction and superconductivity, making them attractive for a new platform to explore functional materials. These compounds have the general chemical formula LnMAX ($Ln = \text{lanthanide}, M = \text{transition metal}, A = \text{chalcogen or pnictogen}, X = O, F \text{ or } H$), which are called “1111-type” compounds and have the tetragonal ZrCuSiAs-type structure (space group $P4/nmm$). In particular, an interesting feature of these compounds is that they have a two-dimensional crystal structure composed of alternating [MA] and [LnX] layers; the former forms a carrier conduction path and the latter forms a wider band gap than the conduction layer and behaves like a carrier transport barrier.

Alternatively, similar layered-structure compounds (i.e., composed of a narrow band gap [MA] layer) have also been found; a representative one is called “122-type” compounds expressed by the chemical formula AeM₂Pn₂ ($Ae = \text{alkaline earth}$). Similar to the 1111-type compounds, the properties of AeM₂Pn₂ change drastically if the type of the transition metal M is varied. For example, AeM₂Pn₂ behave as superconductors (for Fe [9,10] and Ni [11]), ferromagnetic metals (for Co [12]), antiferromagnetic metals (for Cr

[13]), diamagnetic metals (for Cu [14]), antiferromagnetic semiconductors (for Mn [15–18]), and nonmagnetic semiconductors (for Zn [19]). Most of them crystallize into the tetragonal ThCr₂Si₂ structure with the space group $I4/mmm$ [20]. On the other hand, BaZn₂As₂ has two crystalline phases; the low-temperature orthorhombic phase α -BaZn₂As₂ [21] (α -BaCu₂S₂-type structure, the space group $Pnma$) and the high-temperature tetragonal phase β -BaZn₂As₂ [22] (the 122-type one, the space group $I4/mmm$) (Fig. 3.1a). Recently, (Ba_{1-x}K_x)(Zn_{1-y}Mn_y)₂As₂ was reported to be a good diluted magnetic semiconductor, in which the tetragonal phase is stabilized by the doping of 10% K or Mn [19].

It is known that the anion–anion chemical bonding influences the ground states of 122-type compounds significantly and is intertwined with the formation of the ferromagnetic quantum critical point and superconductivity [23,24]. In Chapter 2, the band gap of β -BaZn₂As₂ was determined to be 0.23 eV [25], which is extremely narrow compared with that of the similar 1111-type compound, LaZnAsO (1.5 eV), [4] although they have similar layered structures where the common [ZnAs] layers are expected to form the band gap for both the conduction band minimum (CBM) and valence band maximum (VBM). The similar difference in the band gap is observed also in the Mn-based compounds (i.e. 0.14 eV for BaMn₂P₂ [15], 1.7 eV for LaMnPO [5], 0.06 eV for BaMn₂As₂ [16], 1.5 eV for LaMnAsO [5], 0.06–0.20 eV for BaMn₂Sb₂ [17,18], 1.0 eV for LaMnSbO [5]). Further it has been reported that simple zinc arsenides have much larger band gaps as well (e.g., 0.99 eV for Zn₃As₂ [26] and 0.98 eV for ZnAs₂ [27]). Recently, first-principles calculations for the α - and β -BaZn₂As₂ phases reported that they have complicated and highly anisotropic electronic structures because of the unusual cation–anion and anion–anion hybridizations [28]; however, it does not provide an

explanation for the extreme narrow band gap of β -BaZn₂As₂.

In this chapter, the chemical origins of the narrow band gap of β -BaZn₂As₂ in comparison with LaZnAsO are discussed based on the chemical bonding nature probed by 6 keV hard X-ray photoemission spectroscopy, hybrid density functional calculations, and the ligand theory. It is found that the anion-anion hybridization between adjacent [ZnAs] layers induces a secondary splitting of the outer orbitals of As atoms and widens the VB. In addition, the *d* orbitals of the heavy alkaline earth Ba ion form a deep conduction band (CB) minimum (CBM) due to the non-bonding nature of the Ba 5*d*_{x²-y²} orbitals. These two factors provide a quantitative explanation for the narrow band gap of β -BaZn₂As₂.

3.2 Computational Details

Density functional theory (DFT) and hybrid DFT (HDFT) calculations were performed using the projector augmented plane-wave method implemented in the Vienna *Ab initio* Simulation Program (VASP 5.3) [29]. The plane wave cutoff energy was set to 345.9 eV. A 5×5×2 *k*-mesh was used for tetragonal β -BaZn₂As₂ and LaZnAsO and a 5×5×3 *k*-mesh was used for trigonal *Ae*Zn₂As₂ crystals (*Ae* =Ba, Sr and Ca). For the exchange-correlation functional, first the local density approximation (LDA) and the Perdew–Burke–Ernzerhof (PBE96) [30] generalized gradient approximation (GGA) functional were examined; however, they underestimated the band gaps of β -BaZn₂As₂ and LaZnAsO (see Table 3.1). Then hybrid functionals were examined and it is found that the HSE06 [31,32] hybrid functional with the standard mixing parameter of 25% for the exact-exchange term provided reasonable results. Before the electronic structure calculations, variable-cell structure relaxations were performed using the respective functionals.

3.3 Results and Discussion

3.3.1 Crystal Structure Difference between β -BaZn₂As₂ and LaZnAsO

Figs. 3.1a and 3.1b show the crystal structures of β -BaZn₂As₂ and LaZnAsO, respectively. The literature structural parameters for β -BaZn₂As₂ [22] and LaZnAsO [33] are summarized in Table 3.1. The structures of the [ZnAs] layers are almost the same between β -BaZn₂As₂ and LaZnAsO, where each (ZnAs₄) tetrahedron is connected with four neighboring (ZnAs₄) tetrahedra by sharing their edges. On the other hand, a distinct difference can be found between these structures in Fig. 3.1c, where the coordination numbers of As atoms around an As atom is plotted as a function of As–As distances, $d_{\text{As–As}}$. The intralayer As–As distances (i.e., d_{in} and d_{out} , as denoted in Fig. 3.1a) are similar between β -BaZn₂As₂ and LaZnAsO (0.410–0.425 nm); whereas, the interlayer As–As distance (d_{inter}) for β -BaZn₂As₂ (0.370 nm) is much shorter than that for LaZnAsO (0.660 nm) owing to the different heights between the Ba ion and the LaO layer.

3.3.2 Electronic Structure Differences between β -BaZn₂As₂ and LaZnAsO

Table 3.1 summarizes the literature and calculated band gaps and lattice parameters for β -BaZn₂As₂ and LaZnAsO. While the LDA and PBE96 GGA functionals underestimated the band gaps, the HSE06 hybrid functional provided reasonable band gap values of 0.23 eV for β -BaZn₂As₂ and 1.38 eV for LaZnAsO, which are fairly close to the experimental values. Besides, the HSE06 also gave better structural parameters than the LDA and the PBE96. Therefore, I use the HSE06 calculation results for the following discussion.

The calculated total and projected densities of states (DOSs) for β -BaZn₂As₂ and LaZnAsO are shown in Figs. 3.2a and 3.2b. The CB of β -BaZn₂As₂ between CBM and CBM + 1.0 eV consists mainly of Ba 5*d* and As 4*d* hybridized with small portion of Zn 4*s* orbitals, which is highly dispersed as seen in the band structure in Fig. 3.2c. The CB of

LaZnAsO between CBM and CBM + 1.0 eV consists mainly of Zn 4s and As 4d orbitals with narrower dispersion as seen in Fig. 3.2d. Both compounds exhibit long CB tails in the total DOSs near CBM. The VB of β -BaZn₂As₂ consists mainly of As 4p orbital slightly hybridized with Zn 4p and Ba 5d orbitals; while that of LaZnAsO consists of As 4p orbitals slightly hybridized with Zn 4p orbitals in the shallow region (VBM to -3.6 eV), and the O 2p orbitals slightly hybridized with As 4p and La 5d orbitals in the deeper region (-3.6 to -6.0 eV). In particular, β -BaZn₂As₂ exhibits a long tail structure in the total DOS from -0.6 eV to the VBM.

From the band structures (Figs. 3.2c and 3.2d), it can be seen that the VB levels are split to four similar energy levels in β -BaZn₂As₂ and LaZnAsO at the Z point, which is mainly explained by the intralayer hybridizations between the As atoms. The two bands marked by the red symbols are bonding (σ) and antibonding (σ^*) σ states of As 4p_z orbitals, respectively; while the other two by the blue symbols are bonding (π) and antibonding (π^*) π states of As (4p_x, 4p_y) orbitals, respectively, as confirmed from the *lm*-decomposed DOSs of As 4p orbitals (the fifth panels of Figs. 3.2a and 3.2b). For β -BaZn₂As₂, each doubly degenerated orbital at the Z point splits into two bands along the *k* vector moving to the Γ point because the adjacent [ZnAs] layers interact with each other and form a bonding state and an antibonding state as indicated by σ_1^* and σ_2^* for example in Fig. 3.2c. For LaZnAsO, each band does not exhibit a significant energy split along the Z- Γ direction (Figure 3.3d), which is strikingly different from β -BaZn₂As₂. A comparison the different VB structures shows that the most significant difference near the VBM is found in the σ_2^* band of β -BaZn₂As₂ formed because of the direct interlayer As 4p_z-As 4p_z anti-bond (see Fig. 3.3a), which is highly dispersed and the maximum energy level exceeds the π_2^* band by 0.36 eV at the Γ point; i.e., As 4p_z mainly forms the *lm*-decomposed DOS of the

shallow VB region as seen in the fifth panel of Fig. 3.2b.

3.3.3 Origins of the Narrow Band Gap: I. Interlayer As–As Hybridization

As discussed above, the Γ point splitting of the VB in β -BaZn₂As₂ (denoted as secondary splitting hereafter) is caused by the direct hybridization between interlayer As atoms (schematically shown in Fig. 3.3a) because of the relatively short d_{inter} (0.370 nm). To further confirm this model, HSE06 calculations were performed for several hypothetical structures of β -BaZn₂As₂ with fixed [ZnAs] layers and varied d_{inter} values, as illustrated in Fig. 3.3a. The obtained band gap versus d_{inter} relation is summarized in Fig. 3.5b, and those band structures and DOSs are shown in Figs. 3.3c and 3.3d, respectively. First, the d_{inter} was decreased slightly from 0.370 to 0.360 nm. The secondary splitting of As 4*p* became wider because of the larger hybridization of the interlayer As atoms, which raised the VBM energy level as shown in the left panel in Fig. 3.3c. As a result, the band gap value is decreased to 0.04 eV. When the d_{inter} was increased to 0.380 nm, the secondary splitting of As 4*p* became smaller due to the reduced interlayer hybridizations, which led to a lowered VBM and an increased band gap of 0.40 eV. By further increasing the d_{inter} to 0.400 nm, the secondary splitting became further smaller and the σ^*_2 band did not pass across the π^*_2 band anymore (the right panel of Fig. 3.3c), which made the VBM structure more similar to that of LaZnAsO. Correspondingly, the “tail” structure near VBM faded away completely as seen in Fig. 3.3d. The resulted band gap was further increased to 0.66 eV. It is also confirmed that further increasing d_{inter} did not increase the band gap significantly. From the d_{inter} dependence of band gap summarized in Fig. 3.3b, it is concluded that the interlayer hybridization between the As 4*p_z* orbitals of adjacent layers is an origin of the narrow band gap in β -BaZn₂As₂, which decreases the band gap by ~0.43 eV (the band gap difference between the actual structure ($d_{\text{inter}} = 0.370$ nm) and that with d_{inter} being 0.400

nm). Here, it should be noted that the d_{inter} value in β -BaZn₂As₂ is shorter than that in LaZnAsO, but much longer than As–As bonds in single-bonded As₂-dimers (0.240–0.260 nm) [34] in such as CaNi₂As₂ [35]. This means that the interlayer hybridization of the As 4*p_z* orbitals in β -BaZn₂As₂ is much weaker than the As₂-dimers and is an intermediate case.

3.3.4 Origins of the Narrow Band Gap: II. Nonbonding Ba 5*d_{x²-y²}* Orbital

As discussed above for the PDOS in Fig. 3.2a, the Ba 5*d* orbitals contribute largely to the CB, in particular to the CBM structure. To examine the role of the Ba 5*d* orbitals on the narrow band gap, *lm*-decomposed DOSs for the five Ba 5*d* orbital (i.e. *d_{xy}*, *d_{xz}*, *d_{yz}*, *d_{x²-y²}* and *d_{z²}*) were further calculated and are shown in the rightmost panel of Fig. 3.2a. It is known well that the energy levels of outer *d* orbitals are split by the coordinating ligands, whose energy splits are understood qualitatively from the ligand symmetry (*D_{4h}* around Ba, as shown in Fig. 3.4a) by the group theory. The energy level of the edges of Ba 5*d* orbitals derived from the ligand theory and the *lm*-decomposed DOSs is schematically shown in Fig. 3.4c. As known from the *lm*-decomposed DOSs, the *d_{x²-y²}* has the lowest energy among the five *d* orbitals, and is even lower than that of Zn 4*s* orbital (the dashed line in Fig. 3.4c), and forms the CBM. As drawn in Fig. 3.4a, the *d_{x²-y²}* wave function extends to the interstitial spaces between the neighboring As 4*p* orbitals, minimizes the charge overlap with the As electrons, lowers its energy level due to the small Coulomb repulsion, and forms the deep CBM. Further, as the Ba 5*d_{x²-y²}*–As 4*p* states are non-bonding states due to the point-group symmetry and the restriction of the translational symmetry at the Ba site, which diminishes the energy upshift due to the antibonding interaction between the Ba 5*d_{x²-y²}* and As 4*p* orbitals and also contributes to the formation of the deep CBM. This is similar to the case of superdegeneration observed e.g. in cubic perovskites; for example, the band gaps of GeO₂ are >6 eV, but that in cubic SrGeO₃ is reduced to 2.7 eV due to the

non-bonding nature of Ge 4s [36].

In contrast, LaZnAsO has a lower ligand symmetry of C_{4v} around La (see Figure 3.6b), and each La 5d orbital cannot avoid hybridization with O 2p and As 4p orbitals, where antibonding interaction raises the CBM. The energy split of La 5d orbitals is much narrower, as seen from the *lm*-decomposed DOSs in the rightmost panel of Figure 3.3b and the derived schematic energy diagram in Figure 3.6d. Besides, the energy levels of La 5d orbitals are also up-shifted significantly and are higher than the Zn 4s level due to the antibonding interaction between the La 5d and the O2p and As 4p orbitals. As a result, La 5d orbitals do not contribute to the CBM structure, and the band gap is mainly formed in the [ZnAs] layer. From the above discussion, it is concluded that the non-bonding Ba $5d_{x^2-y^2}$ orbital forms the deep CBM and contributes to the narrow band gap of β -BaZn₂As₂.

3.4 Conclusions

The HSE06 calculations, which reproduce the experimental band gap values and the VB structures of β -BaZn₂As₂ and LaZnAsO, revealed that the extremely narrow band gap in β -BaZn₂As₂ originates from two reasons; one is the pushed-up VBM which is primarily composed of antibonding states of As 4p_z orbitals in the adjacent layers, and the other is the extremely low-lying energy level of the non-bonding Ba $5d_{x^2-y^2}$ orbitals, which is lower even than Zn 4s states. It is believed that the present results provide a clue to better understanding of the evolution of band structure and flexible control of band gap and carrier transport in versatile pnictide compounds.

References

- [1] K. Ueda, S. Inoue, S. Hirose, H. Kawazoe, and H. Hosono, Appl. Phys. Lett. **77**, 2701 (2000).

- [2] H. Hiramatsu, K. Ueda, H. Ohta, M. Hirano, T. Kamiya, and H. Hosono, *Appl. Phys. Lett.* **82**, 1048 (2003).
- [3] K. Kayamura, H. Hiramatsu, M. Hirano, R. Kawamura, H. Yanagi, T. Kamiya, and H. Hosono, *Phys. Rev. B* **76**, 195325 (2007).
- [4] K. Kayamura, R. Kawamura, H. Hiramatsu, H. Yanagi, M. Hirano, T. Kamiya, and H. Hosono, *Thin Solid Films* **516**, 5800 (2008).
- [5] K. Kayanuma, H. Hiramatsu, T. Kamiya, M. Hirano, and H. Hosono, *J. Appl. Phys.* **105**, 073903 (2009).
- [6] Y. Kamihara, H. Hiramatsu, M. Hirano, R. Kawamura, H. Yanagi, T. Kamiya, and H. Hosono, *J. Am. Chem. Soc.* **128**, 10012 (2006).
- [7] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, *J. Am. Chem. Soc.* **130**, 3296 (2008).
- [8] T. Watanabe, H. Yanagi, Y. Kamihara, T. Kamiya, M. Hirano, and H. Hosono, *J. Solid State Chem.* **181**, 2117 (2008).
- [9] M. Rotter, M. Tegel, and D. Johrendt, *Phys. Rev. Lett.* **101**, 107006 (2008).
- [10] T. Katase, H. Hiramatsu, H. Yanagi, T. Kamiya, M. Hirano, and H. Hosono, *Solid State Commun.* **149**, 2121 (2009).
- [11] E. D. Bauer, F. Ronning, B. L. Scott, and J. D. Thompson, *Phys. Rev. B* **78**, 172504 (2008).
- [12] D. J. Singh, A. S. Sefat, M. A. McGuire, B. C. Sales, and D. Mandrus, *Phys. Rev. B* **79**, 094429 (2009).
- [13] A. S. Sefat, D. J. Singh, R. Jin, M. A. McGuire, B. C. Sales, and D. Mandrus, *Phys. Rev. B* **79**, 024512(2009).
- [14] V. K. Anand, P. K. Perera, A. Pandey, R. J. Goetsch, A. Kreyssig, and D. C. Johnston,

- Phys. Rev. B **85**, 214523 (2012).
- [15] S. L. Brock, J. E. Greedan, and S. M. Kauzlarich, J. Solid State Chem. **113**, 303 (1994).
- [16] Y. Singh, A. Ellern, and D. C. Johnston, Phys. Rev. B **79**, 094519 (2009).
- [17] H. F. Wang, K. F. Cai, H. Li, L. Wang, and C. W. Zhou, J. Alloys Compd. **477**, 519 (2009).
- [18] J. An, A. S. Sefat, D. J. Singh, and M. -H. Du, Phys. Rev. B **79**, 075120 (2009).
- [19] K. Zhao, Z. Deng, X. C. Wang, W. Han, J. L. Zhu, X. Li, Q. Q. Liu, R. C. Yu, T. Goko, B. Frandsen, L. Liu, F. Ning, Y. J. Uemura, H. Dabkowska, G. M. Luke, H. Luetkens, E. Morenzoni, S. R. Dunsiger, A. Senyshyn, P. Böni, and C. Q. Jin, Nat. Commun. **4**, 1442 (2013).
- [20] G. Just and P. J. Paufler, Alloys Compd. **232**, 1 (1996).
- [21] P. Klüfers and A. Mewis, Z. Naturforsch. **33b**, 151 (1978).
- [22] A. Hellmann, A. Löhken, A. Wurth, and A. Mewis, Z. Naturforsch. **62b**, 155 (2007).
- [23] S. Kawasaki, T. Tabuchi, X. F. Wang, X. H. Chen, and G. -Q. Zheng, Supercond. Sci. Technol. **23**, 054004 (2010).
- [24] S. Jia, P. Jiramongkolchai, M. R. Suchomel, B. H. Toby, J. G. Checkelsky, N. P. Ong, and R. J. Cava, Nat. Phys. **7**, 207 (2011).
- [25] Z. Xiao, F.-Y. Ran, H. Hiramatsu, S. Matsuishi, H. Hosono, and T. Kamiya, Thin Solid Films **559**, 100 (2014).
- [26] J. Misiewicz and J. M. Pawlikowski, Solid State Commun. **32**, 687 (1979).
- [27] A.V. Mudryi, A. I. Patuk, I. A. Shakin, A. E. Kalmykov, S. F. Marenkin, and A. M. Raukhan, Mater. Chem. Phys. **44**, 151 (1996).
- [28] I. R. Shein and A. L. Ivanovskii, J. Alloys Compd. **583**, 100 (2014).

- [29] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [30] J. P. Perdew, K. Burke, and M. Ernzerhof, *M. Phys. Rev. Lett.* **77**, 3865 (1996).
- [31] J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **118**, 8207 (2003).
- [32] J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **124**, 219906 (2006).
- [33] H. Lincke, R. Glaum, V. Dittrich, M. H. Möller, and R. Z. Pöttgen, *Anor. Allg. Chem.* **635**, 936 (2009).
- [34] R. Hoffmann and C. Zheng, *J. Phys. Chem.* **89**, 4175 (1985).
- [35] R. Poble, R. Frankovsky, and D. Z. Johrendt, *Naturforsch.* **68b**, 581 (2013).
- [36] H. Mizoguchi, T. Kamiya, S. Matsuishi, and H. Hosono, *Nat. Commun.* **2**, 470 (2011).

Table 3.1. Experimental and calculated band gaps (E_g) and structural parameters of β -BaZn₂As₂ and LaZnAsO. “Exp.” indicates literature values, and “LDA”, “PBE96” and “HSE06” are those obtained by DFT/HDFT calculations using these functionals. Δ show the deviations from the experimental values.

Compound	Method	E_g (eV)	a (Å) / Δ (%)	c (Å) / Δ (%)	V (Å ³) / Δ (%)
β -BaZn ₂ As ₂	Exp.	0.23 [25]	4.12 [22]	13.578 [22]	230.49 [22]
	LDA	< 0	4.043 / -1.9	13.205 / -2.7	215.89 / -6.3
	PBE96	< 0	4.168 / +1.2	13.630 / +0.4	236.75 / +2.7
	HSE06	0.23	4.151 / +0.7	13.616 / +0.3	234.64 / +1.8
LaZnAsO	Exp.	1.50 [4]	4.0956 [33]	9.07 [33]	152.13 [33]
	LDA	0.36	4.018 / -1.9	8.828 / -2.7	142.53 / -6.3
	PBE96	0.56	4.113 / +0.4	9.126 / +0.7	154.38 / +1.4
	HSE06	1.38	4.098 / +0.0	9.099 / +0.4	152.78 / +0.4

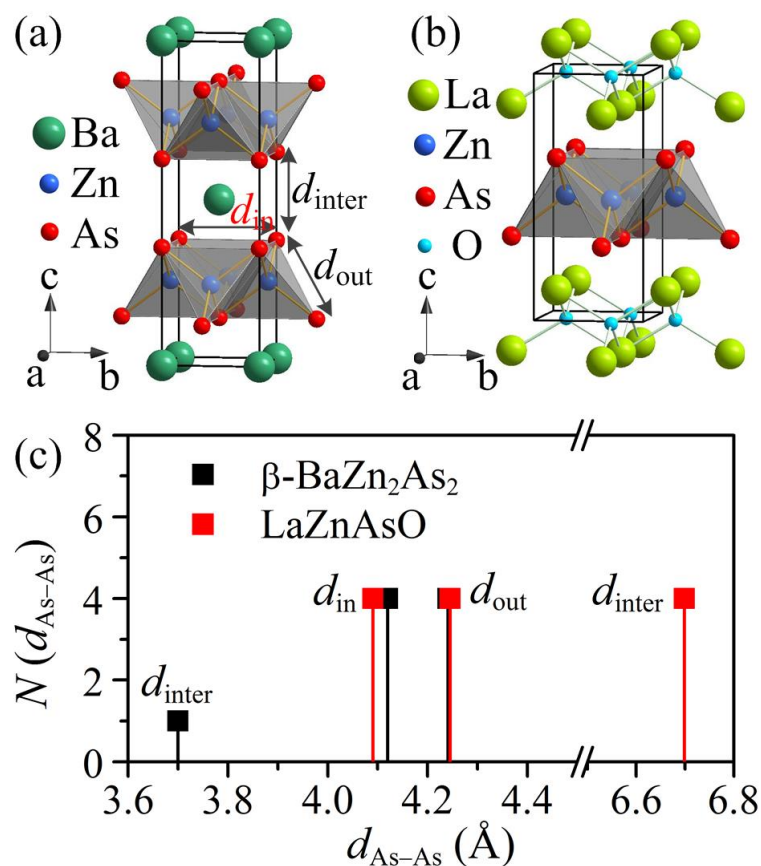


Figure 3.1. Crystal structures. Schematic illustrations for (a) β -BaZn₂As₂ ($I4/mmm$) and (b) LaZnAsO ($P4/nmm$). The d_{in} (equal to the lattice parameter a), d_{out} and d_{inter} parameters are defined as the distances between the nearest As neighbors along the in-plane, the out-of-plane and the interlayer directions, respectively, as denoted in (a). (c) Comparison of coordination structures among β -BaZn₂As₂, LaZnAsO, and tri-BaZn₂As₂, which plots the coordination number distribution of As atoms around an As atom as a function of As-As distance (d_{As-As}). Reprinted with permission from [J. Am. Chem. Soc. 2014, 136, 14959–14965](#). Copyright 2014 American Chemical Society.

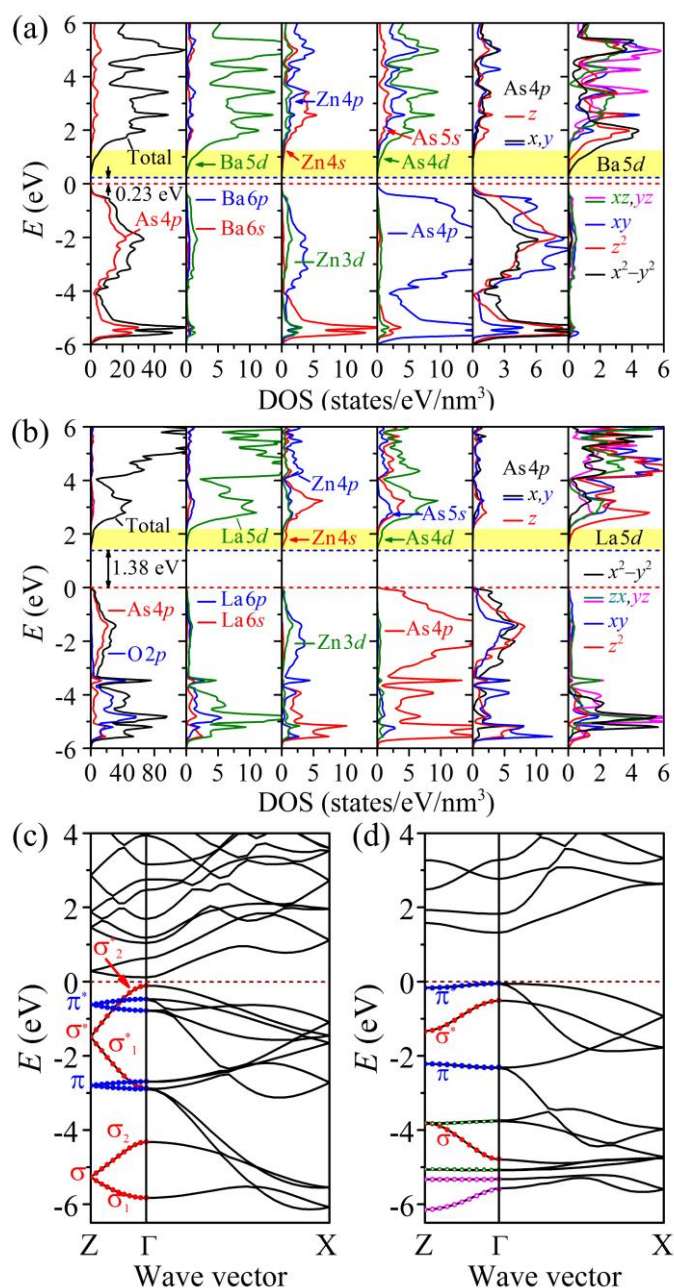


Figure 3.2. (a and b) Total, projected, and lm -decomposed densities of states (DOS) of (a) β -BaZn₂As₂ and (b) LaZnAsO. The red and blue lines mark the valence band maximum (VBM) and the conduction band minimum (CBM), respectively. (c and d) Band structures of (c) β -BaZn₂As₂ and (d) LaZnAsO. The dashed lines mark the VBMs. Reprinted with permission from [J. Am. Chem. Soc. 2014, 136, 14959–14965](#). Copyright 2014 American Chemical Society.

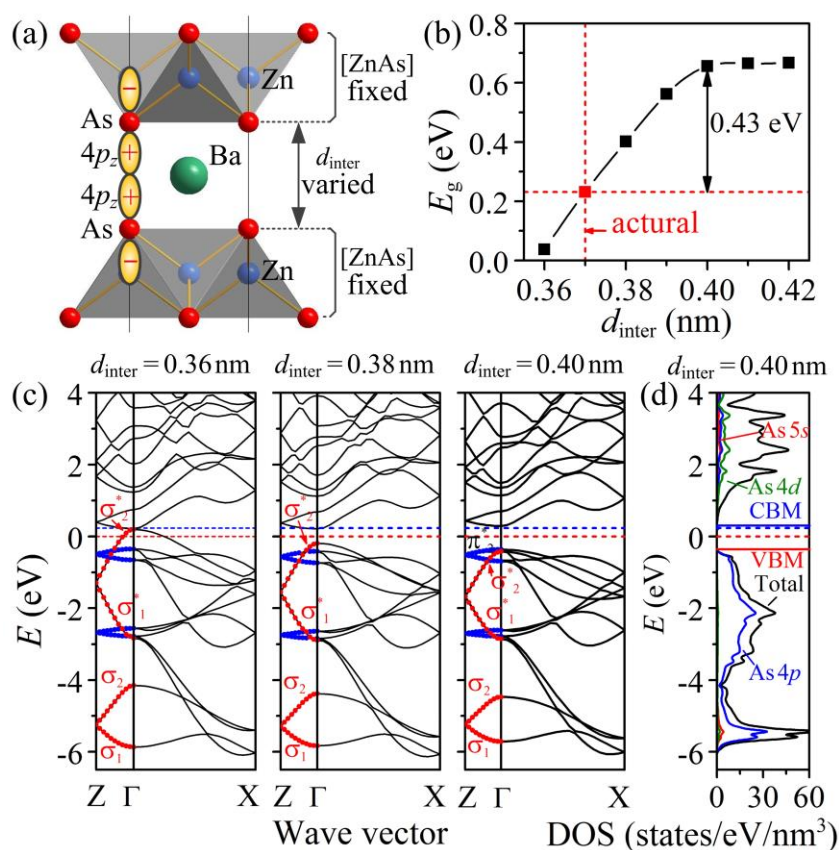


Figure 3.3. (a) Schematic illustration of hypothetical structures of β -BaZn₂As₂ with fixed [ZnAs] layer structures and varied d_{inter} values. (b) Calculated band gap of β -BaZn₂As₂ as a function of d_{inter} . (c) Band structures of hypothetical β -BaZn₂As₂ structures with d_{inter} being 0.36, 0.38 and 0.40 nm. (d) Total and projected DOSs of hypothetical β -BaZn₂As₂ with $d_{\text{inter}} = 0.40$ nm. In (c) and (d), the energies are aligned to the energy levels of the Zn 3d orbitals, and the dashed red and blue lines mark the VBM and the CBM of the experimental β -BaZn₂As₂ structure ($d_{\text{inter}} = 0.37$ nm) for comparison. Reprinted with permission from [J. Am. Chem. Soc. 2014, 136, 14959–14965](#). Copyright 2014 American Chemical Society.

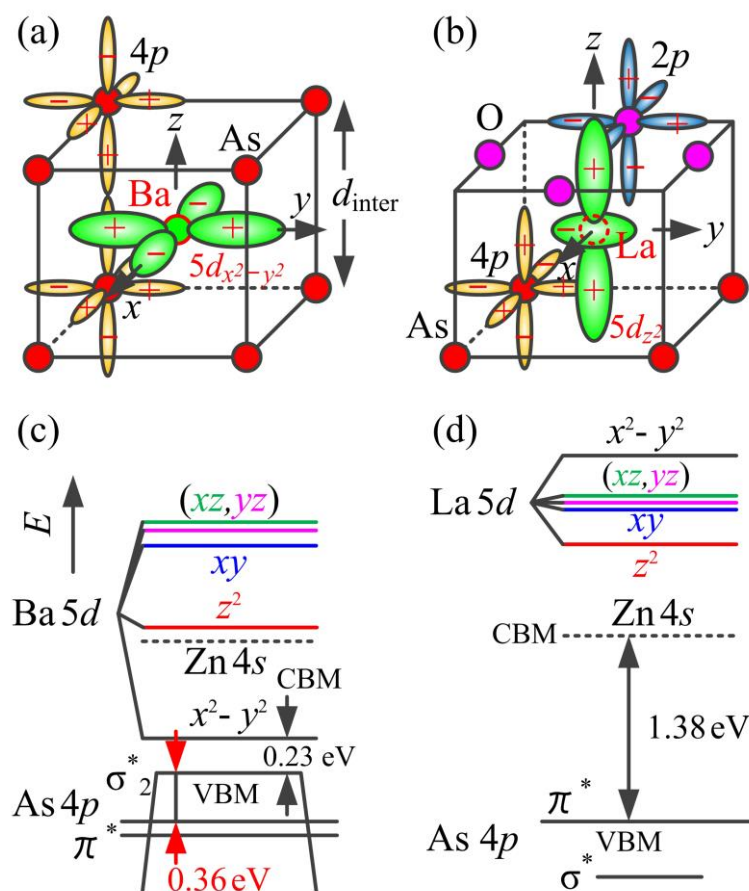


Figure 3.4. (a,b) Ligand geometries of (a) D_{4h} around Ba in β -BaZn₂As₂ and (b) C_{4v} around La in LaZnAsO. The wave functions of the As 4p orbitals, the O 2p orbitals and the lowest 5d orbitals of Ba and La are also shown schematically. (c,d) Schematic energy diagrams near the VBM and the CBM for (c) β -BaZn₂As₂ and (d) LaZnAsO. The energy levels are derived from the lm -decomposed DOSs in Figs. 3(a,b) and aligned by Zn 3d levels. Reprinted with permission from [J. Am. Chem. Soc. 2014, 136, 14959–14965](#). Copyright 2014 American Chemical Society.

Chapter 4

Origins of Doping Asymmetry in SnS

4.1 Introduction

Control of carrier polarity conversion in semiconductor is important to produce high-performance semiconductor devices such as solar cells and light emitters, and is actually utilized in conventional semiconductors such as Si and compound semiconductors. On the other hand, it is known that such bipolar doping is not attained easily in other semiconductors; e.g., most of oxide semiconductors are of naturally *n*-type, and it is difficult to obtain *p*-type conduction in the same materials as known e.g. for SnO₂, and vice versa e.g. for Cu₂O and NiO. To date, several, but a limited number of doping routes have been recognized and employed. For ionic semiconductors, aliovalent ion substitution and off-chemical stoichiometry are known well; e.g., substitution of Zn²⁺ with Ga³⁺ increased the electron density in ZnO [1], and Cu vacancy increased the hole density in Cu₂O [2]. Further, H doping is now recognized as an important and effective route for *n*-type doping in oxide semiconductors [3]. For organic semiconductors and devices, chemical doping, which is caused by partial charge transfer originating from different electron affinities of constituent atoms / functional groups, is important [4]. The most popular route for carrier polarity conversion is aliovalent ion substitution; actually, *n*-type conversion of SnO was realized by substituting Sb³⁺ ions for the Sn²⁺ ions [5]. However, up to now, this route has not been succeeded in many semiconductors, such as SnS.

SnS is a naturally *p*-type semiconductor with hole densities of 10^{15} – 10^{18} cm⁻³ and the high mobilities ~ 90 cm²/(Vs) [6,7]. It has a layered crystal structure along the *a*-axis direction as shown in Fig. 1a, which belongs to the orthorhombic lattice (the space group *Pnma*, No. 62). Due to its reasonable small bandgap of ~ 1.07 eV [8] and strong optical absorption coefficients above the bandgap ($> 10^5$ cm⁻¹), SnS is expected to be a promising absorber material for low-cost thin-film solar cells. Thus, numerous *n*-type materials, including CdS [9,10], SnS₂ [11], FeS₂ [12], TiO₂ [13], ZnO [14], and amorphous Si [15], have been employed for fabricating heterojunction SnS-based solar cells. However, the highest energy conversion efficiency reported up to now is limited to $\sim 3.88\%$ [16,17], which is much lower than the theoretically-predicted value of 24% [18]. The low efficiency might suffer from unfavorable band alignments and the large lattice mismatches in the heterojunction structures [19,20]. Fabricating a homojunction solar cell with *p*-SnS/*n*-SnS structure would solve this problem.

With this line, much effort has been devoted to obtaining *n*-type SnS materials by substituting the Sn²⁺ ions with aliovalent ions with the charge state of 3+. Dussan *et al.* report that Bi³⁺-doped SnS exhibits *n*-type conduction when the Bi concentration is larger than 50% [21]. Whereas, a Bi₂S₃ impurity phase, which is also *n*-type, was observed in their heavily Bi-doped SnS films [22]. Sajeeshesh *et al.* claim that *n*-type SnS thin films are obtained by chemical spray pyrolysis, but their result might be due to a significant *n*-type Sn₂S₃ impurity phase in the films [23]. Very recently, Sinsermsuksakul *et al.* tried to obtain *n*-type SnS by Sb³⁺ doping; however, except for great increase in the electrical resistance of the SnS film, no *n*-type conduction was observed [24]. To date, no reliable *n*-type SnS material has yet been reported. That is, SnS suffers the doping asymmetry problem; i.e., it can be naturally doped *p*-type, but hardly *n*-type, which hinders the

fabrication of *p*-SnS/*n*-SnS homojunction for high-performance solar cells.

In this chapter, the defect physics of SnS was investigated by defect calculations based on density functional theory (DFT). Particularly, the origins of the doping asymmetry in SnS were discussed based on the DFT calculation results and the band alignment diagram. Further, aliovalent Sb³⁺ and Bi³⁺ doping in SnS was also theoretically assessed.

4.2 Computational Details

The electronic structure and defect calculations were performed for SnS in the framework of DFT using the projector augmented plane-wave method as implemented in the VASP code [25]. The local density approximation (LDA) was used for the exchange-correlation functional, as employed in Ref. [26]. The plane-wave cut-off energy was set to 323.3 eV. A 72-atom supercell and a 3×3×3 Monkhorst-Pack *k*-mesh were used. Prior to the electronic and the total energy calculations, internal ion coordinate parameters were optimized so as to take the minimum total energy but the supercell parameters were fixed (the fixed-cell structural relaxations) so as to meet the dilute limit condition [27]; that is, the lattice parameters were constrained to the experimental values (i.e., $a = 11.18 \text{ \AA}$, $b = 3.982 \text{ \AA}$, $c = 4.329 \text{ \AA}$ [28]). It is known that the total energies for defect-containing models, in particular for charged defects, are affected by considerable finite-size effects [29]. Therefore, the common posteriori corrections to the calculated total energies were applied by the methodology in the literatures [29,30].

The formation enthalpy ($\Delta H_{D,q}$) of a defect (*D*) in a charge state *q* is calculated through the equation [27]

$$\Delta H_{D,q}(E_F, \mu) = E_{D,q} - E_H - \sum n_\alpha \mu_\alpha + q(E_F + E_V + \Delta V), \quad (4.1)$$

where $E_{D,q}$ and E_H are the total energies of a supercell with a defect in the charge state *q*

and a perfect host supercell, respectively. n_α indicates the number of α atoms added to ($n_\alpha > 0$) or removed from ($n_\alpha < 0$) the defect supercell model, and μ_α is the chemical potential of an α atom with respect to that of an elemental phase (μ_α^{el}) given by $\mu_\alpha = \mu_\alpha^{\text{el}} + \Delta\mu_\alpha$. E_F is the Fermi level relative to the valence band maximum (VBM, E_V) which is corrected by the ΔV method [27]. μ_α varies depending on the experimental condition during growth or annealing where the defect states are frozen and ranges from the S-rich (Sn-poor) to the S-poor (Sn-rich) conditions. $\Delta\mu_\alpha$ should satisfy the thermal equilibrium stability conditions; i.e., $\Delta\mu_{\text{Sn}} + \Delta\mu_{\text{S}} = \Delta H(\text{SnS})$. The S-rich conditions are given by the equilibrium conditions between SnS and Sn₂S₃; while the S-poor limit is taken with respect to elementary β -Sn (i.e. $\Delta\mu_{\text{Sn}} = 0$).

The defect concentrations $c_{D,q}$ are calculated by the statistic equation [27]

$$c_{D,q}(E_F, \mu, T_D) = N_{D,q} \exp[\Delta S_{D,q}/k_B - \Delta H_{D,q}(E_F, \mu)/k_B T_D], \quad (4.2)$$

where $N_{D,q}$ is the concentration of the possible sites where the defects can be formed, $\Delta S_{D,q}$ the formation entropy, k_B the Boltzmann constant, and T_D the growth or annealing temperature (i.e., the defects formed at T_D were assumed to be frozen to room temperature). It is difficult to determine $\Delta S_{D,q}$ by DFT; therefore a typical value of $5k_B$ [31] was used for defects in SnS. The equilibrium Fermi level ($E_{F,e}$), $c_{D,q}$ and the net carrier concentration for given μ and T_D were determined so as to satisfy the charge neutrality condition [31].

4.3 Results and Discussion

4.3.1 Properties of Intrinsic Defects in SnS

The calculated ΔH of the intrinsic defects in SnS (vacancies V_{Sn} and V_{S} , interstitials Sn_i and S_i , and antisites Sn_{S} and S_{Sn}) are shown in Figs. 5.2a and 5.2b for the S-rich and S-poor conditions, respectively. Under both conditions, V_{Sn} has the lowest ΔH with a shallow

$\alpha(0/2-)$ transition at 0.03 eV above the VBM, which is close to the experimental observation (0.22 eV) [32] and mainly responsible for the p -type conduction in SnS. This result substantiates the established experimental observations theoretically [33,34]. Under the S-poor condition, Sn_S has a low ΔH comparable to that of V_{Sn}, and but acts as a deep acceptor because it is ionized to negative only in the high E_F region ≥ 0.36 eV. V_S and Sn_i have $\alpha(n+/0)$ transition levels closer to the VBM than to the conduction band minimum (CBM, $E_C = E_V + E_g$, where E_g is the band gap 1.08 eV); i.e, they work as donors but the $\alpha(n+/0)$ levels are far below the CBM and cannot be n -type sources. S_{Sn} and S_i have too large ΔH to affect the electrical properties. These results are consistent with those reported in Ref. 26.

Figures 4.2c and 4.2d show the calculated c_D of the dominant defects at $T = 673.15$ K (the deposition temperature in Ref. 8) under the S-rich and S-poor conditions, respectively. In the S-rich condition, $E_{F,e}$ was calculated to be 0.07 eV from the VBM by the charge neutrality condition. At $E_{F,e}$, the acceptor V_{Sn}²⁻ are generated at the high c_D of 1.4×10^{18} cm⁻³, but compensated slightly by the generation of the donor V_S²⁺ (2.0×10^{15} cm⁻³) and S_{Sn}⁺ (2.4×10^{11} cm⁻³), thus yielding the net hole concentration (p) of 2.7×10^{18} cm⁻³. Under the S-poor condition, $E_{F,e}$ is increased to 0.41 eV from the VBM. The holes produced by V_{Sn}²⁻ ($2 \times 3.9 \times 10^{15}$ cm⁻³) and Sn_S⁻ (5.2×10^{15} cm⁻³) are partially compensated by the electrons produced by V_S²⁺ ($2 \times 2.0 \times 10^{15}$ cm⁻³), resulting in the lowered p of 7.6×10^{15} cm⁻³. These results are in good agreement with our previous experimental results in epitaxial SnS films [8]; i.e., p ranged from 4.0×10^{15} to 2.2×10^{17} cm⁻³, as well as the theoretical results by Vidal *et al* [26].

4.3.2 Origins of Doping Asymmetry in SnS

Since no intrinsic defect can be an effective n -type source as shown above, it is unlikely to

obtain intrinsic n -type doping in pure SnS under all growth conditions (i.e. from the S-rich to the S-poor). Further, the extrinsic dopability also can be perceived from the results shown in Fig. 4.1. Under S-rich condition, V_{Sn}^{2-} has negative ΔH at n -type conditions (i.e., $E_F > E_g/2$) and will form spontaneously and accept the electrons released by n -type dopants. Therefore, n -type doping is impossible under S-rich condition. On the other hand, under S-poor condition, V_{Sn}^{2-} has positive but very small ΔH at some n -type conditions. Therefore, n -type doping is possible but would be difficult because the compensating V_{Sn}^{2-} also form heavily. These results substantiate the doping asymmetry in SnS, i.e., it is readily doped p -type, but not n -type.

The origins of doping asymmetry in SnS can also be understood qualitatively based on the band alignment diagram shown in Fig. 4.2a. It is known that Si has moderate ionization potential (IP) of 5.17 eV and moderate electron affinity (EA) of 4.05 eV [35]; therefore, can be readily doped either p -type by B dopant or n -type by P dopant. PbS, which is of the rocksalt structure, has a smaller IP (4.95 eV) and a larger EA (4.54 eV) than Si [36], and exhibit either p -type conduction or n -type conduction without extrinsic doping. For SnS, the IP and EA were determined to be 4.68 and 3.60 eV, respectively, from the UPS spectra of an SnS film shown in Fig. 4.2b (i.e. a work function of 4.20 eV and an E_F of 0.48 eV) and the band gap of 1.08 eV [8]. The IP of SnS is much smaller than Si and PbS, indicating the holes generated are more energetically stable. As a result, SnS intrinsically exhibit p -type conduction. On the other hand, SnS has too small EA , the electrons doped are energetically unstable, causing the n -type doping difficulty.

The origins of small IP and EA values in SnS can be explained by the formation of the VBM and CBM structure. For most metal sulfide semiconductors such as SnS₂, the VBM is mainly composed of S 3p orbitals while the CBM is mainly composed of s orbitals of

metal cation. For SnS (see the bottom of Fig. 4.2c), the Sn 5s orbitals are fully occupied and have shallow energy levels close to the S 3p orbitals; therefore, they couple with each other and form bonding states at 5–8 eV and antibonding states at 10.5–12.5 eV (note that the energy is referred to the S 3s levels). The VBM of SnS is composed of the S 3p–Sn 5s antibonding states. It should be noted that the VBM of SnS is pushed up by the strong coupling between S 3p and Sn 5s, and higher than the typical sulfide semiconductors. On the other hand, the CBM of SnS is mainly composed of Sn 5p–S 3p antibonding states. Similarly, the Sn 5p–S 3p coupling pushes up the CBM to a shallow energy level. Therefore, it is concluded that the shallowness of the VBM and the CBM are caused by the strong *s*–*p* and *p*–*p* couplings between Sn²⁺ cation and S²⁻ anion.

In contrast, PbS has much deeper VBM and CBM than SnS (see Fig. 4.2a), though they are family compounds. The difference would originate from the different crystal structures and/or different metal cations, where the latter is of more interest for materials design. Therefore, herein, a hypothetical orth-PbS (*Pnma*, the same as SnS), rather than the real cubic one (rocksalt structure), is compared. The calculated electronic structure of orth-PbS is shown in the top of Fig. 4.2c. As it can be clearly seen, Pb 6s orbitals are much deeper than Sn 5s orbitals, which may be attributed to the relativistic effect in the heavy metal [37]. As a result, the *sp* coupling in orth-PbS is much weaker than that in SnS. As a result, the VBM of orth-PbS is 0.53 eV deeper than that of SnS. Similarly, the CBM of orth-PbS is 0.45 eV deeper than that of SnS, which is explained by the deeper energy levels of Pb 6p orbitals than Sn 5p orbitals also due to the relativistic effect [37]. One may expect that *n*-type doping would be easier in orth-PbS if it really exists and that the serious doping asymmetry problem in SnS would be improved if Pb is incorporated in the SnS lattice. The effects of Pb substitution in SnS will be discussed in the following Chapter 5.

4.3.3 Assessment of Sb³⁺ and Bi³⁺ Doping in SnS

Aliovalent ion doping by Sb³⁺ and Bi³⁺ into the Sn²⁺ sites, which are expected to release electrons for *n*-type conductivity [21,24], but has not been effective. Here, the Sb and Bi doping effects are theoretically assessed by defect calculations. Three possible doping sites, i.e. the Sn substitutional sites (Sb_{Sn} and Bi_{Sn}), the antisites on S (Sb_S and Bi_S), and the interstitial sites (Sb_i and Bi_i) were examined. The calculated ΔH are shown in Figs. 5.3a and 5.3b. The Sb and Bi dopants can hardly be incorporated to the interstitial sites because of the prohibitively high ΔH values (> 2 eV) of Sb_i and Bi_i. Under the S-rich condition, the Sb_{Sn} and Bi_{Sn} have lower ΔH than the Sb_S and Bi_S and are energetically favored. The Sb_{Sn} and Bi_{Sn} have the $\alpha(+/0)$ transition levels at 0.74 and 0.71 eV, respectively, and would work as deep donors. However, V_{Sn}²⁻ has lower ΔH in the E_F region closer to the CBM, indicating that the holes produced by V_{Sn}²⁻ are not compensated completely by the electrons generated from Sb_{Sn} and Bi_{Sn}. As a result, the resulting *p* is decreased by 1–2 orders of magnitude with increasing the dopant content (the blue lines in Figs. 5.3c and 5.3d, which explains the observed result that the resistivity increased by 2 orders of magnitude in the Sb-doped SnS thin films by Sinsermsuksakul *et al.* [24].

On the other hand, the S-poor condition is favored to suppress the formation of V_{Sn} acceptors. However, under the S-poor condition, Sb and Bi prefer to take the Sn sites at low E_F (acting as donors) as expected but unexpectedly the S sites at high E_F (acting as acceptors). The resulting $E_{F,e}$ are pinned at 0.43 and 0.48 eV from the VBM for the cases of Sb and Bi dopants, respectively. The resulting *p* is almost independent of the dopant content as seen in the red lines in Figs. 5.3c and 5.3d.

From these results, it would be unlikely to achieve *n*-type conductivity in SnS by aliovalent doping using the Sb and Bi dopants. On the other hand, Dussan *et al.* [21]

claimed that *n*-type conduction was obtained in SnS by Bi substitution. However, *n*-type SnS₂ and Bi₂S₃ impurity phases were detected in their films, which would be a possible origin of the observed *n*-type conductivity.

4.4 Conclusions

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 compensate *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 Sn²⁺ cation and S²⁻ anion, respectively. Further, Sb and Bi doping in SnS was assessed and found not effective to attain *n*-type conduction in SnS.

References

- [1] H. J. Ko, Y. F. Chen, S. K. Hong, H. Wensch, T. Yao and D. C. Look, *Appl. Phys. Lett.* **77**, 3761 (2000).
- [2] H. Raebiger, S. Lany, and A. Zunger, *Phys. Rev. B* **76**, 045209 (2007).
- [3] L.-Y. Chen, W.-H. Chen, J.-J. Wang, F. C.-N. Hong and Y.-K. Su, *Appl. Phys. Lett.* **85**, 5628 (2004).
- [4] H. Méndez, G. Heimel, A. Opitz, K. Sauer, P. Barkowski, M. Oehzelt, J. Soeda, T. Okamoto, J. Takeya, J.-B. Arlin, J.-Y. Balandier, Y. Geerts, N. Koch, and I. Salzmann, *Angew. Chem. Int. Edit.* **52**, 7751 (2013).
- [5] H. Hosono, Y. Ogo, H. Yanagi, and T. Kamiya, *Solid-State Lett.* **14**, H13 (2011).
- [6] W. Albers, C. Haas, and F. van der Maesen, *Phys. Chem. Solids* **15**, 306 (1960).

- [7] N. R. Mathews, H. B. M. Anaya, M. A. Cortes-Jacome, C. Angeles-Chavez, and J. A. Toledo-Antonio, *J. Electrochem. Soc.* **157**, H337 (2010).
- [8] F.-Y. Ran, Z. Xiao, H. Hiramatsu, H. Hosono, and T. Kamiya, *Appl. Phys. Lett.* **104**, 072106 (2014).
- [9] K. T. Ramakrishna Reddy, N. Koteswara Reddy, and R. W. Miles, *Sol. Energy Mater. Sol. Cells* **90**, 3041 (2006).
- [10] S. A. Bashkirov, V. F. Gremenok, V. A. Ivanov, V. V. Lazenka, and K. Bente, *Thin Solid Films* **520**, 5807 (2012).
- [11] A. Sánchez-Juárez, A. Tiburcio-Silver, and A. Ortiz, *Thin Solid Films* **480**, 452 (2005).
- [12] N. Berry, M. Cheng, C. L. Perkins, M. Limpinsel, J. C. Hemminger, and M. Law, *Adv. Energy Mater.* **2**, 1124 (2012).
- [13] Y. Wang, H. Gong, B. H. Fan, and G. X. Hu, *J. Phys. Chem. C* **114**, 3256 (2010).
- [14] M. Ichimura and H. Takagi, *Jpn. J. Appl. Phys.* **47**, 7845 (2008).
- [15] F. Jiang, H. L. Shen, W. Wang, and L. Zhang, *J. Electrochem. Soc.* **159**, H235 (2012).
- [16] P. Sinsersuksakul, K. Hartman, S. B. Kim, J. Heo, L. Sun, H. H. Park, R. Chakraborty, T. Buonassisi, and R. G. Gordon, *Appl. Phys. Lett.* **102**, 053901 (2013).
- [17] V. Steinmann, R. Jaramillo, K. Hartman, R. Chakraborty, R. E. Brandt, J. R. Poindexter, Y. S. Lee, L. Sun, A. Polizzotti, H. H. Park, R. G. Gordon, and T. Buonassisi, *Adv. Mater.* **26**, 7488 (2014).
- [18] A. Schneikart, H.-J. Schimper, A. Klein, and W. Jaegermann, *J. Phys. D. Appl. Phys.* **46**, 305109 (2013).
- [19] L. Sun, R. Haight, P. Sinsersuksakul, S. Bok Kim, H. H. Park, and R. G. Gordon, *Appl. Phys. Lett.* **103**, 181904 (2013).

- [20] X. Cai, S. Zeng, and B. Zhang, *Appl. Phys. Lett.* **95**, 173504 (2009).
- [21] A. Dussan, F. Mesa, and G. Gordillo, *J. Mater. Sci.* **45**, 2403 (2010).
- [22] G. Gordillo, M. Botero, and J. S. Oyola, *Microelectron. J.* **39**, 1351 (2008).
- [23] T. H. Sajeesh, A. R. Warriar, C. S. Kartha, and K. P. Vijayakumar, *Thin Solid Films* **518**, 4370 (2010).
- [24] P. Sinsermsuksakul, R. Chakraborty, S. B. Kim, S. M. Heald, T. Buonassisi, and R. G. Gordon, *Chem. Mater.* **24**, 4556 (2012).
- [25] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [26] J. Vidal, S. Lany, M. d’Avezac, A. Zunger, A. Zakutayev, J. Francis, and J. Tate, *Appl. Phys. Lett.* **100**, 032104 (2012).
- [27] C. G. Van De Walle and J. Neugebauer, *J. Appl. Phys.* **95**, 3851 (2004).
- [28] S. Del Bucchia, J.-C. Jumas, and M. Maurin, *Acta Crystallogr.* **B37**, 1903 (1981).
- [29] S. Lany and A. Zunger, *Phys. Rev. B* **78**, 235104 (2008).
- [30] S. Lany and A. Zunger, *Model. Simul. Mater. Sci. Eng.* **17**, 084002 (2009).
- [31] D. B. Laks, C. G. Van de Walle, G. F. Neumark, P. E. Blöchl, and S. T. Pantelides, *Phys. Rev. B* **45**, 10965 (1992).
- [32] T. H. Sajeesh, K. B. Jinesh, M. Rao, C. S. Kartha, and K. P. Vijayakumar, *Phys. Status Solidi A* **209**, 1274 (2012).
- [33] A. Lichanot and S. Gromb, *J. Phys. Chem. Solids* **32**, 1947 (1971).
- [34] M. Devika, K. T. R. Reddy, N. K. Reddy, K. Ramesh, R. Ganesan, E. S. R. Gopal, and K. R. Gunasekhar, *J. Appl. Phys.* **100**, 023518 (2006).
- [35] S. M. Sze and K. K. Ng, *Physics of Semiconductor Devices* (John Wiley & Sons, Inc., Hoboken, New Jersey, 2007).
- [36] S. A. McDonald, G. Konstantatos, S. Zhang, P. W. Cyr, E. J. D. Klem, L. Levina, and E. H. Sargent, *Nat. Mater.* **4**, 138 (2005).

- [37] P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong, *Inorganic Chemistry*, 5th ed. (Oxford University Press, New York, 2010).

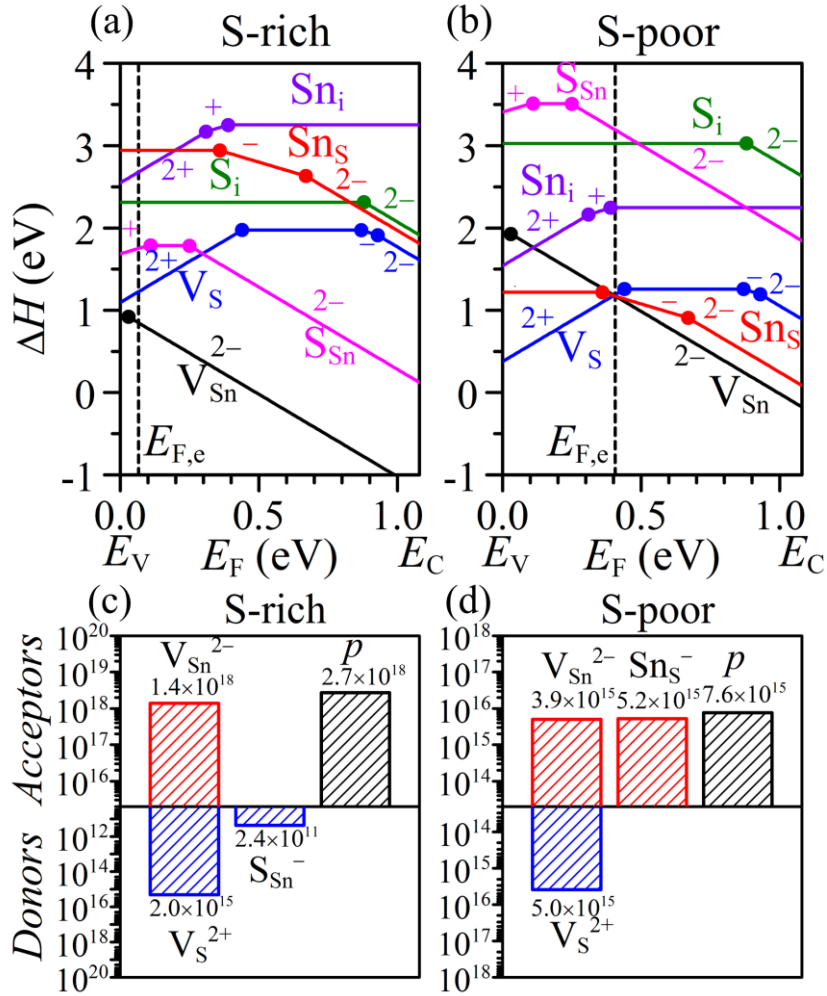


Figure 4.1. (a,b) Calculated formation enthalpies ΔH for intrinsic point defects in SnS as a function of E_F under (a) S-rich and (b) S-poor conditions. The vertical dashed lines mark the equilibrium Fermi level $E_{F,e}$ at $T = 673.15$ K. (c,d) Calculated defect concentrations in cm^{-3} at $T = 673.15$ K under (c) S-rich and (d) S-poor conditions. The black hatched bars show the equilibrium net carrier concentrations in cm^{-3} .

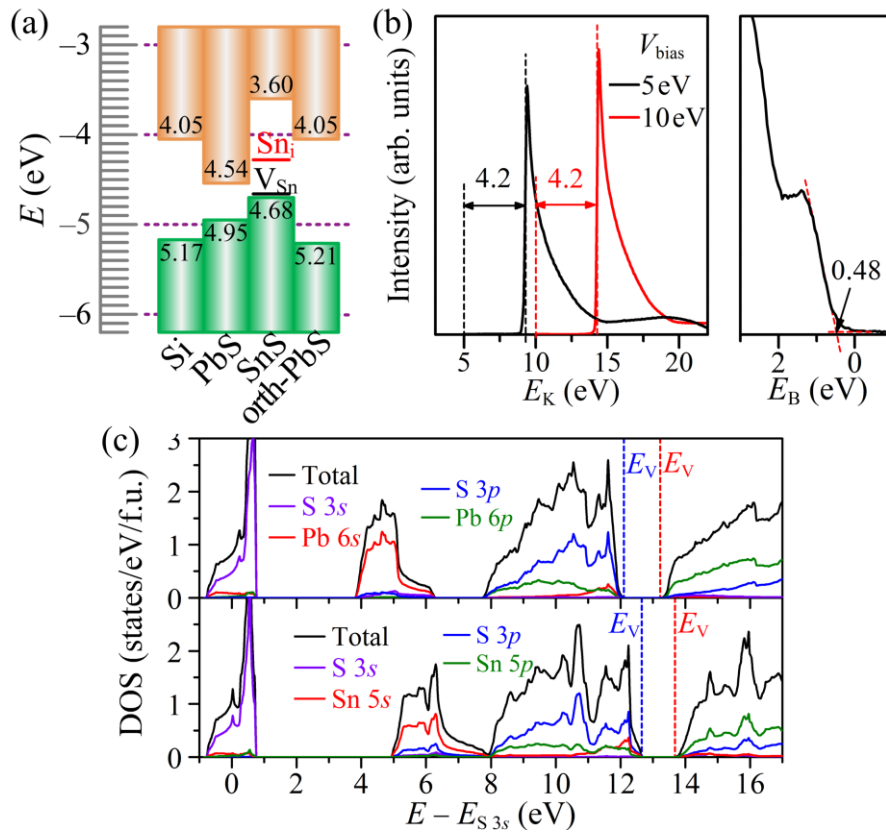


Figure 4.2. (a) Band alignment between Si [35], PbS [36], SnS and hypothetical orth-PbS (space group $Pnma$, isostructural to SnS). The data of SnS and orth-PbS were obtained from USP spectra shown in (b) and DFT calculation shown in (c), respectively. (b) UPS spectra of an epitaxial SnS film [8]. (c) Total and projected densities of states (DOSs) of SnS (bottom panel) and orth-PbS. The energies are aligned with referring to the Sn 3s orbitals.

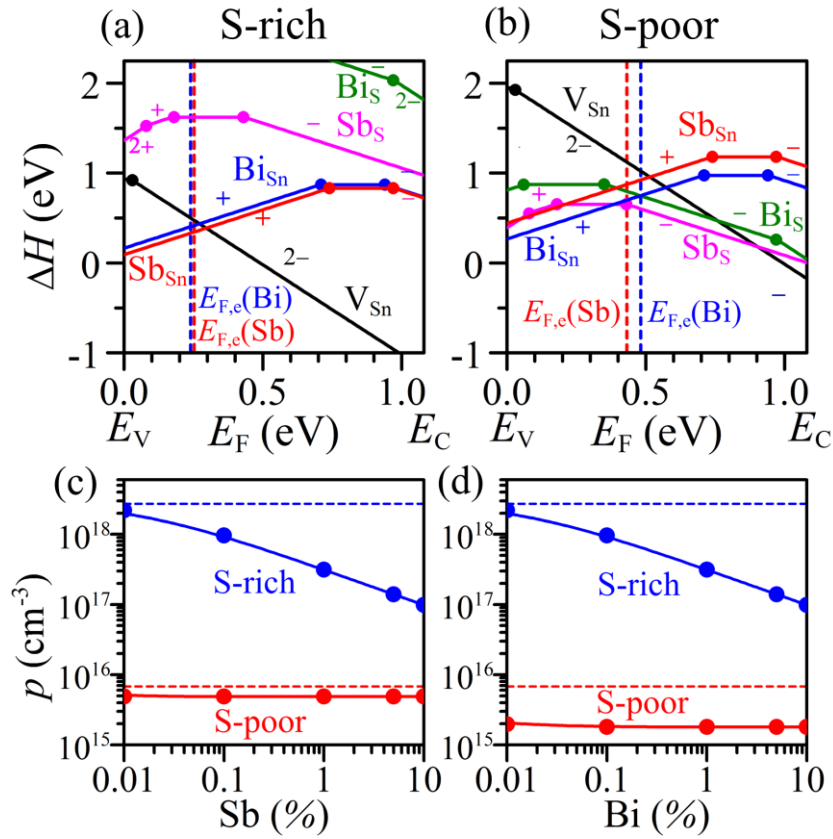


Figure 4.3. (a,b) Calculated formation enthalpies ΔH for Sb and Bi impurities in SnS as a function of E_F under (a) S-rich and (b) S-poor conditions. Also included is the dominant intrinsic defect V_{Sn} for comparison. The vertical dashed lines mark the $E_{F,e}$ at $T = 673.15$ K for 5% dopants. (c,d) Calculated carrier concentrations as functions of the dopant concentrations of (c) Sb and (d) Bi under S-rich (blue solid lines) and S-poor (red solid lines) conditions. The dashed lines mark the equilibrium carrier concentrations for the intrinsic defects in the undoped SnS for comparison.

Chapter 5

n-Type Conversion of SnS by Geometrical Doping Route

5.1 Introduction

In [Chapter 4](#), the doping asymmetry in SnS are explained by the too small ionization potential (*IP*) and electron affinity (*EA*) (i.e., the shallow VBM and CBM levels) based on defect calculation and band alignment. The small *IP* makes that the holes are energetically favored and readily generated by the intrinsic defect V_{Sn} in SnS. On the other hand, the small *EA* makes the doped electrons in SnS unstable, causing the *n*-type doping difficulty in SnS. The density functional theory (DFT) calculations suggest that the shallow VBM and CBM are originated from the shallow occupied Sn 5*s* and unoccupied Sn 5*p* orbitals (see [Chapter 4](#) for details). On the other hand, hypothetical orth-PbS has deeper VBM and CBM levels than SnS, because the Pb 6*s* and 6*p* orbitals are deeper than the Sn 5*s* and 5*p* orbitals due to the relativistic effect [1]. Based on these understandings, it is reasonable to expect that incorporating Pb into SnS lattice would deepen the VBM and CBM levels, and thus improve or even solve the doping difficulty in SnS.

In this chapter, reliable *n*-type conduction was achieved in SnS films fabricated isovalent Pb^{2+} doping. It is found that the doping mechanism is strikingly different from the conventional doping routes such as ion substitution, off-stoichiometry, and chemical doping. 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.

5.2 Experimental and Computational Details

5.2.1 Fabrication and Characterization

(Sn_{1-x_f}Pb_{x_f})S films (x_f is film chemical composition) were grown on SiO₂ glass substrates by pulsed laser deposition (PLD) using a KrF excimer laser (248 nm in wavelength, 3–6 J/cm² of laser energy density, and 10 Hz of repetition rate) in an Ar / H₂S mixing gas flow (80 / 20 %) to control the chemical stoichiometry ([Sn]+[Pb]) : [S] (the parentheses denote the concentrations). (Sn_{1-x_t}Pb_{x_t})S (x_t is target chemical composition) polycrystalline disks with $x_t = 0.18, 0.37, \text{ and } 0.66$ were used as ablation targets. The base pressure of the growth chamber was 1×10^{-5} Pa, the substrate temperature (T_s) was varied from 200 to 400 °C, and the mixing gas pressure (P) from 5 to 20 Pa.

The crystalline phase and crystal structure of the obtained films were characterized by X-ray diffraction (XRD, radiation source = Cu K α). Optical properties were obtained by measuring transmittance (T_r) and reflectance (R) spectra. The absorption coefficient (α) was estimated by $\alpha = \ln[(1-R)/T_r] / t$, where t is the film thickness. Electrical properties of the SnS films were analyzed by Hall effect measurements using the van der Pauw configuration with an AC modulation of magnetic field. x_f values were determined by X-ray fluorescence (XRF) spectroscopy calibrated by the chemical compositions obtained by inductively-coupled plasma-atomic emission spectroscopy (ICP-AES). The valence band structures were observed by UPS (excitation source = He I, 21.2 eV), where the films were protected in an Ar atmosphere during the transfer from the PLD chamber to the UPS chamber.

5.2.2 Theoretical Calculations

Stable crystal / defect structures, their electronic structures, and formation energies of intrinsic defects were calculated by density functional theory (DFT) calculations with local density approximation (LDA) and generalized gradient approximation (GGA) functionals using the VASP code [2]. The plane wave cutoff energy was set to 323.3 eV. A 32-atoms substitutional (Sn_{16-n}Pb_n)S₁₆ model (1×2×2 unit cells) model and a 4×6×5 *k*-mesh were used for the calculations of structural properties and electronic structures. The defect calculations were performed using a 64-atoms (Sn₁₆Pb₁₆)S₃₂ model and a 3×3×3 *k*-mesh. The detailed procedures for calculating the defect formation enthalpy (ΔH) and equilibrium Fermi level ($E_{F,e}$) are the same as described in Chapter 4.

5.3 Results and Discussion

5.3.1 Structural properties of (Sn_{1-x_f}Pb_{x_f})S films

Figure 5.1a shows a typical out-of-plane $2\theta/\omega$ synchronous scan (top panel) and an in-plane synchronous $2\theta_\chi/\phi$ scan (bottom panel) XRD patterns of the (Sn_{1-x_f}Pb_{x_f})S film with $x_f = 0.5$ grown at substrate temperature (T_s) = 300 °C and $P = 5$ Pa. The out-of-plane XRD pattern exhibited strong 200, 400 and 800 diffractions of the orthorhombic structure along with a weak 011 diffraction. The in-plane synchronous $2\theta_\chi/\phi$ scan (bottom panel) shows powder-like patterns with all possible *hkl* diffractions, suggesting that the film did not have in-plane orientation. These results indicate that the (Sn_{1-x_f}Pb_{x_f})S films were polycrystalline films with a strong 100 preferential orientation normal to the substrate. No impurity phase was detected both in the out-of-plane and the in-plane XRD patterns. As seen in Figs. 5.1b and 5.1c, orthorhombic (Sn_{1-x_f}Pb_{x_f})S films were obtained at $P < 20$ Pa (corresponding to the closed symbols in Fig. 5.2a); while, amorphous films were obtained

when P was increased to 20 Pa (the open symbols in Fig. 5.2a).

The lattice parameters of $(\text{Sn}_{1-x_f}\text{Pb}_{x_f})\text{S}$ films obtained from the out-of-plane 400 and the in-plane 020 and 011 diffraction angles are summarized as a function of x_f in Fig. 5.1d. As x_f increased from 0 to 0.5, the a and b values increased linearly from 1.12 to 1.14 nm and from 0.403 to 0.414 nm, respectively, whereas the c value decreased from 0.426 to 0.419 nm; i.e., the interlayer distance (corresponding to the a value) increased. The solid lines in Fig. 5.1d represent the lattice parameters of the $(\text{Sn}_{1-x}\text{Pb}_x)\text{S}$ bulk sample reported by Leute *et al.* [3]. The a values of the films are almost the same as those of the bulk samples. However, the b and c values exhibited non-negligible deviations from the bulk values; i.e., the b -axis was expanded while the c -axis shrunken compared from the bulk values. The reason is not clear, but defects in the polycrystalline films would cause the structural difference. Figure 5.1d also compares the variation of the lattice parameters with those obtained by DFT calculations (the open symbols) performed with the $(\text{Sn}_{16-n}\text{Pb}_n)\text{S}_{16}$ supercell model (Pb substitution model). Here, both LDA and GGA functionals are compared. It can be seen that the calculated results for the Pb substitution model were within the variation of the functionals (typically, the ground-state lattice parameters by DFT include errors within 2–3%). That is, this model, where the Sn sites are substituted by Pb, explains the experimental structure well, and strongly supports that the Pb dopants are successfully incorporated to the Sn sites in the SnS lattice.

5.3.2 Electrical Properties of $(\text{Sn}_{1-x_f}\text{Pb}_{x_f})\text{S}$ films

Figure 5.2a shows the variation of x_f as functions of P , T_s and x_t . It is seen that all the x_f values were smaller than the x_t values of the corresponding targets, and the x_f values decreased with increasing P . As seen for the target with $x_t = 0.37$, the maximum x_f of Pb was incorporated when the films were grown at $T_s = 300$ °C, which, therefore, was

employed hereafter for discussion. The crystallized region in Fig. 5.2a is classified further to three regions based on the electrical properties. Region I is “*p*-type region” (high $P \geq 15$ Pa at low $x_f < 0.1$), where the films still exhibited *p*-type conduction with low hole densities (N_h) and low hole mobilities (μ_h) (measured by Hall effect). *n*-type ($\text{Sn}_{1-x_f}\text{Pb}_{x_f}$)S films were obtained in Region II (“*n*-type region”, $x_f \geq 0.15$ at low $P \leq 10$ Pa). The electron density (N_e) and mobility (μ_e) changed largely with x_f and P , which will be discussed later on. Region III is the intermediate region (“highly-resistive region”, low x_f & low P , and high x_f & high P), where the films exhibited very high resistivity $>10^5 \Omega \cdot \text{cm}$, and the Hall effect measurements did not give definite Hall voltage signs.

The detailed Hall effect measurement results as a function of x_f are shown in Fig. 5.2b. The pure SnS film showed *p*-type conduction with $N_h \sim 4.1 \times 10^{15} \text{ cm}^{-3}$ and $\mu_h \sim 12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The ($\text{Sn}_{1-x_f}\text{Pb}_{x_f}$)S film with $x_f = 0.08$ fabricated at $P = 15$ Pa still showed *p*-type conduction but with the low $N_h \sim 1.0 \times 10^{14} \text{ cm}^{-3}$ and the very small μ_{Hall} in the order of $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. When $x_f \geq 0.2$, *n*-type conduction was observed for the films fabricated at $P = 5$ and 10 Pa. For the *n*-type ($\text{Sn}_{1-x_f}\text{Pb}_{x_f}$)S film with $x_f = 0.2$, N_e and μ_e were $1.4 \times 10^{12} \text{ cm}^{-3}$ and $1.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. N_e increased with increasing x_f and reached $2.0 \times 10^{15} \text{ cm}^{-3}$ for $x_f = 0.5$. μ_e was not changed largely when $x_f < 0.3$ ($N_e < 3.2 \times 10^{13} \text{ cm}^{-3}$). At x_f values > 0.4 , μ_e increased almost linearly, and the maximum value of $7.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was obtained for $x_f = 0.5$.

Figure 5.2c shows temperature dependences of N_e and μ_e for the ($\text{Sn}_{1-x_f}\text{Pb}_{x_f}$)S film with the room-temperature N_e of $4.3 \times 10^{13} \text{ cm}^{-3}$ ($x_f = 0.48$ grown at 10 Pa). The N_e shows a thermally-activated behavior with an active energy of $E_a \sim 0.4 \text{ eV}$. From a simple approximation in the impurity region $N_e = (N_D N_C)^{1/2} \exp[-(E_C - E_D)/(2k_B T)]$ (N_D is the donor density, N_C the conduction band effective density of states (DOS), $E_C - E_D$ the donor

level measured from the conduction band minimum E_C , k_B the Boltzmann constant), $E_C - E_D$ and N_D are estimated to be ~ 0.8 eV and $2.5 \times 10^{21} \text{ cm}^{-3}$ ($N_C = 2.8 \times 10^{21} \text{ cm}^{-3}$ is taken from Si), respectively. On the other hand, although E_F was closer to E_C as in usual *n*-type semiconductors, the donor level E_D was closer to the valence band maximum energy (E_V) rather than E_C , showing that the *n*-type doping in the $(\text{Sn}_{1-x}\text{Pb}_x)\text{S}$ films is a bit different from the usual *n*-type semiconductors.

As shown by the red line in Fig. 5.2c, μ_e decreased with decreasing the temperature, and the $\ln(\mu_{\text{Hall}} T^{1/2}) - T^{-1}$ plot exhibited a good straight line in the whole T range, suggesting that the electron transport in the film was dominated by grain boundary (GB) potential barriers as proposed by Seto *et al.* [4], where electron transport is disturbed by potential barriers formed due to the electrons trapped at acceptor-type defects at the GBs. The GB potential barrier height E_B is estimated to be approximately 0.09 eV (the equation [4] is given in Fig. 5.2c). From this result, the potential electron mobility μ_0 (i.e., the ideal value when no GB affects the carrier transport) was estimated to be $\sim 1.6 \times 10^2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ by extrapolating E_B to zero (i.e., $\mu_0 = \mu_{\text{Hall}} \exp(E_B/kT)$).

Further, *n*-type $(\text{Sn}_{0.5}\text{Pb}_{0.5})\text{S}$ / *p*-type Si pn heterojunction (see the inset of Fig. 5.2d) was prepared to confirm the *n*-type conduction in $(\text{Sn}_{1-x}\text{Pb}_x)\text{S}$ films. The *n*- $(\text{Sn}_{0.5}\text{Pb}_{0.5})\text{S}$ film and the *p*-Si wafer used had $N_e = 2 \times 10^{15}$ and $N_h = 5 \times 10^{15} \text{ cm}^{-3}$, respectively. The current–voltage (I – V) characteristic of the pn junction (Fig. 5.2d) shown a clear rectifying characteristic, further supporting the *n*-type conduction of the $(\text{Sn}_{1-x}\text{Pb}_x)\text{S}$ films.

5.3.3 Electronic Structure and Band Alignment of $(\text{Sn}_{0.5}\text{Pb}_{0.5})\text{S}$

Figures 5.3a and 5.3b show typical optical absorption spectra and $(\alpha h\nu)^{1/2} - h\nu$ plots (the indirect-transition model) of the $(\text{Sn}_{1-x}\text{Pb}_x)\text{S}$ films fabricated at the various conditions, respectively. The pure SnS film (the black line in Fig. 5.3a) exhibited very weak subgap

absorption, and the bandgap estimated from $(\alpha hv)^{1/2} - hv$ plot is 1.08 eV. The band gaps (E_g) estimated from Fig. 5.3b are shown in Fig. 5.3c as a function of x_f , showing that the E_g increased with increasing x_f , and reached to 1.15 eV for $x_f = 0.5$. The calculated E_g values with LDA and GGA are also shown in Fig. 5.3c. As it can be seen, the GGA reproduces the experimental E_g values better than the LDA.

Figure 5.3d shows the valence band spectrum of the $(\text{Sn}_{0.5}\text{Pb}_{0.5})\text{S}$ film measured by UPS. The observed E_F of the $(\text{Sn}_{0.5}\text{Pb}_{0.5})\text{S}$ film was located at 0.82 eV above VBM. From the E_g of 1.15 eV, the $E_C - E_F$ value is estimated to be 0.33 eV, closer to conduction band maximum (CBM), agreeing with *n*-type conduction. Figure 5.3e shows the UPS spectra with bias voltages (V_{bias}) of 5 and 10 V. From the relative cutoff energy of the secondary electrons, the work function (W) of the $(\text{Sn}_{0.5}\text{Pb}_{0.5})\text{S}$ film was determined to be 4.20 eV. From the above results (i.e., $W = 4.2$ eV, $E_F = 0.82$ eV, and $E_g = 1.15$ eV), the ionization potential ($IP = W + E_F$) and electron affinity ($EA = IP - E_g$) of the $(\text{Sn}_{0.5}\text{Pb}_{0.5})\text{S}$ films were estimated to be 5.02 and 3.87 eV, respectively.

Figure 5.3f shows band alignment between Si [5], PbS [6], SnS, $(\text{Sn}_{0.5}\text{Pb}_{0.5})\text{S}$ and hypothetical orth-PbS (see details in Chapter 4). As clearly seen, $(\text{Sn}_{0.5}\text{Pb}_{0.5})\text{S}$ has moderate IP and EA values (5.02 and 3.87 eV, respectively) between those of SnS (4.68 and 3.60 eV, respectively) and those of orth-PbS (5.21 and 4.05 eV, respectively). These results indicate that incorporating Pb in SnS increased both the IP and the EA , as expected. This change can be explained by comparing the electronic structures of SnS and $(\text{Sn}_{0.5}\text{Pb}_{0.5})\text{S}$, as shown in the top and the bottom of Fig. 5.3g, respectively. As has been discussed in Chapter 4, the shallow VBM (i.e. the small IP) and CBM (i.e. the small EA) are attributed to the strong Sn $5s$ -S $3p$ coupling and the shallow energy levels of Sn $5p$ orbitals, respectively (the top of Fig. 5.3g). As seen from the projected DOSs of $(\text{Sn}_{0.5}\text{Pb}_{0.5})\text{S}$ (the bottom of Fig. 5.3g),

the Pb 6s orbitals are deeper than the Sn 5s orbitals, making the *sp* coupling in (Sn_{0.5}Pb_{0.5})S weaker than pure SnS and thus the VBM deeper (i.e. the *IP* larger). Similarly, the Pb 6p orbitals are deeper than the Sn 5p orbitals, making the CBM of (Sn_{0.5}Pb_{0.5})S deeper than pure SnS (i.e. the *EA* larger).

5.3.4 Microscopic Mechanism of *n*-Type Doping by Pb Substitution

It should be emphasized that the *n*-type conduction in the (Sn_{1-*x*}Pb_{*x*})S films was achieved by isovalent substitution of Sn²⁺ by Pb²⁺, and the doping mechanism cannot be explained by the conventional concept of aliovalent ion doping. To reveal the *n*-type doping mechanism in (Sn_{1-*x*}Pb_{*x*})S, defect calculations were performed for (Sn_{0.5}Pb_{0.5})S, as a representative of (Sn_{1-*x*}Pb_{*x*})S. Note that S-poor condition is favored for *n*-type doping in SnS to suppress the formation of tin vacancies (V_{Sn}), as discussed in Chapter 4, and the *n*-type (Sn_{1-*x*}Pb_{*x*})S films were indeed obtained only when grown under S-poor conditions (i.e., at low H₂S pressures). Therefore, the S-poor condition was employed for the following discussion.

Figure 5.4a shows the calculated ΔH of intrinsic defects along with those of Pb impurities in SnS. The detailed discussion for intrinsic defects in SnS has been given in Chapter 4. Here, it should be noted that V_{Sn} is a shallow acceptor responsible for the native *p*-type conduction with an $\varepsilon(2-/0)$ transition at 0.03 eV above the VBM, and that Sn interstitial (Sn_i) is a deeper donor with an $\varepsilon(+/0)$ transition at 0.68 eV below the CBM. For Pb impurities in SnS, three possible sites (i.e. Pb_{Sn} substitutional site, Pb_S antisite, and Pb_i interstitial site) were examined. Among them, Pb_{Sn} has the lowest ΔH which is slightly below zero and is stabilized in the neutral state, indicating Pb substitution of Sn may occur spontaneously to form (Sn_{1-*x*}Pb_{*x*})S solid solutions and does not accept or release electrons.

Figure 5.4b shows the calculated ΔH for intrinsic defects in (Sn_{0.5}Pb_{0.5})S. It can be seen that ΔH of V_{Sn}²⁻ increased significantly compared with that in pure SnS, which is

mainly caused by the lower chemical potential of Sn in (Sn_{0.5}Pb_{0.5})S. Besides, V_{Sn} in (Sn_{0.5}Pb_{0.5})S has deep $\varepsilon(n-/0)$ transitions at around 0.31 eV above the VBM, which is 0.28 eV deeper than that in pure SnS. As illustrated in Fig. 5.3f, V_{Sn} has similar absolute energy levels in SnS and (Sn_{0.5}Pb_{0.5})S. Because the VBM (Sn_{0.5}Pb_{0.5})S was lowered by the Pb substitution, V_{Sn} relatively became deeper. In (Sn_{0.5}Pb_{0.5})S, V_{Pb} has comparable ΔH with V_{Sn}, but shallower transition levels.

On the other hand, the ΔH of Sn_i²⁺ in (Sn_{0.5}Pb_{0.5})S was largely reduced compared with that in pure SnS, and the $\varepsilon(2+/+)$ and $\varepsilon(+/0)$ transitions of Sn_i became much shallower, at 0.11 and 0.02 eV below the CBM, respectively. As illustrated in Fig. 5.3f, the shallowing of Sn_i transition levels by 0.66 eV is only partly caused by the reduction of CBM by 0.27 eV and there should be other more important causes. It should be noted the interlayer distance (corresponding to the *a*-axis length) and the *b*-axis lattice parameters were increased by the Pb substitution, as shown in Fig. 5.1d. These geometrical alternations reduce ΔH of Sn_i²⁺ by about 0.78 eV (i.e. $2 \times (0.66 - 0.27)$ eV, where 2 is the charge number) and make the formation of Sn²⁺ much easier. Similarly, Pb_i²⁺ acts as shallow donor, but has slightly larger ΔH (by 0.15 eV) than Sn_i²⁺ due to the larger ionic radius of Pb²⁺ than that of Sn²⁺.

For quantitative analysis, the equilibrium E_F ($E_{F,e}$) of (Sn_{0.5}Pb_{0.5})S at 300 °C (i.e., the defect structures at the growth temperature were assumed to be frozen to room temperature) was calculated by considering all the ΔH values and the semiconductor statistics, giving $E_{F,e} - E_V = 0.71$ eV with $[V_{Sn}^{2-}] = 5.5 \times 10^{13}$, $[V_{Pb}^{2-}] = 4.6 \times 10^{14}$, $[Sn_i^{2+}] = 6.1 \times 10^{14}$, and $[Pb_i^{2+}] = 3.2 \times 10^{13}$ cm⁻³. Note that the V_S has the charge neutral state at this $E_{F,e}$, and does not contribute to charge doping. Consequently, the free holes were generated at 1.0×10^{15} cm⁻³, while the larger amounts of free electrons were generated at 1.3×10^{15}

cm^{-3} , resulting in *n*-type doping. Finally, it is concluded that Sn_i and Pb_i are the most plausible origins of the *n*-type conduction in the $(\text{Sn}_x\text{Pb}_{1-x})\text{S}$ films.

5.4 Conclusions

In summary, *n*-type conduction in SnS was achieved by isovalent Pb substitution with the maximum electron mobility of $7 \text{ cm}^2/(\text{Vs})$. The Pb substitution reduced the VBM and CBM, and thus reduced the severity of the doping asymmetry. More importantly, the substitution invoked a geometrical size effect that enlarges the interlayer distance and subsequently induces the formation of Sn and Pb cation interstitials, which result in the electron doping. The present finding provides a novel idea for carrier doping. Even keeping the same crystal structure and the ion charges, easiness of impurity doping, in particular for atoms / ions with largely-different sizes, depends significantly on the lattice parameters and the internal atomic coordinates, which can be altered also by impurity doping. Further, although substitution doping usually requires aliovalent ion doping to alter the carrier polarity or concentration, geometrical doping has more flexibility because isovalent ion doping would also work for carrier doping.

References

- [1] P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong, *Inorganic Chemistry*, 5th ed. (Oxford University Press, New York, 2010).
- [2] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [3] V. Leute, A. Behr, C. Hünting, and H. M. Schmidtke, *Solid State Ionics* **68**, 287 (1994).
- [4] J. Y. W. Seto, *J. Appl. Phy.* **46**, 5247 (1975).
- [5] S. M. Sze and K. K. Ng, *Physics of Semiconductor Devices* (John Wiley & Sons, Inc.,

Hoboken, New Jersey, 2007).

- [6] S. A. McDonald, G. Konstantatos, S. Zhang, P. W. Cyr, E. J. D. Klem, L. Levina, and E. H. Sargent, *Nat. Mater.* **4**, 138 (2005).
- [7] J. Vidal, S. Lany, M. d'Avezac, A. Zunger, A. Zakutayev, J. Francis, and J. Tate, *Appl. Phys. Lett.* **100**, 032104 (2012).

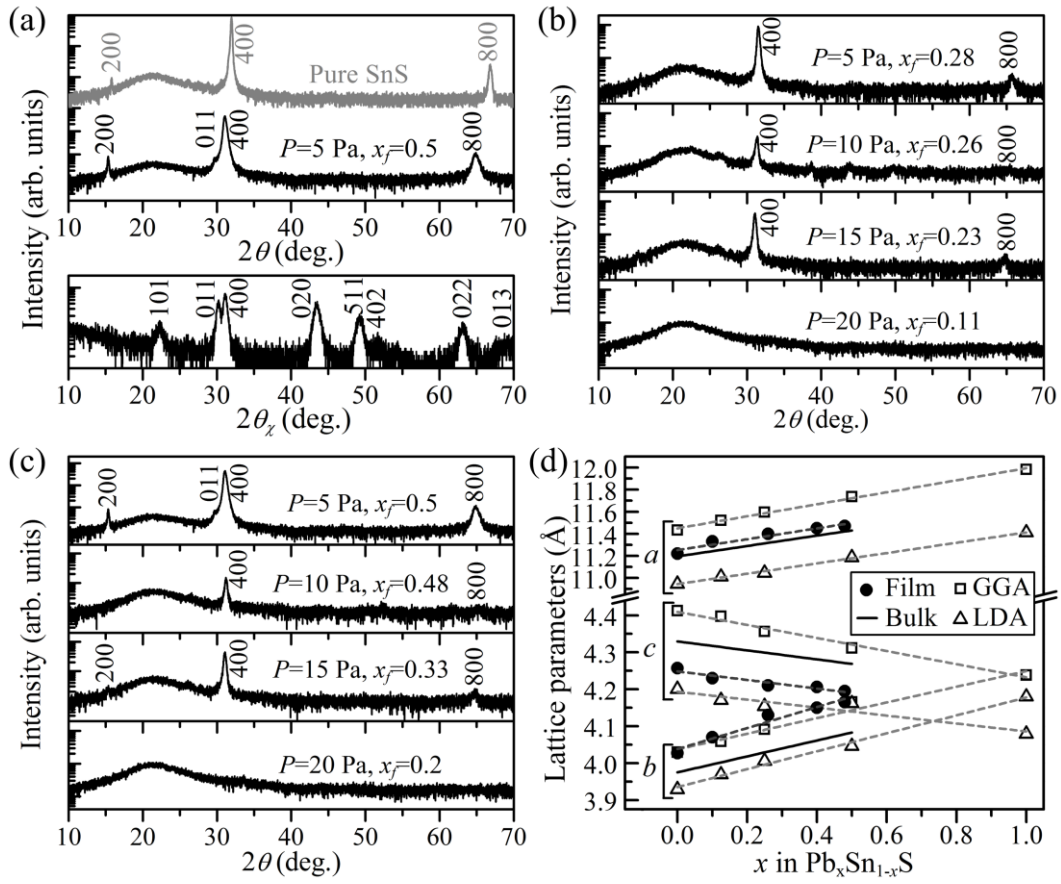


Figure 5.1. Structural properties of $(\text{Sn}_{1-x}\text{Pb}_x)\text{S}$ films. (a) Typical out-of-plane (top panel) and in-plane (bottom panel) XRD patterns of $(\text{Sn}_{1-x}\text{Pb}_x)\text{S}$ film with $x_f=0.5$ grown at 300 °C and 5 Pa. (b and c) XRD patterns of the $(\text{Sn}_{1-x}\text{Pb}_x)\text{S}$ films grown at 300 °C with various conditions. (d) Lattice parameters (a , b , c) of $(\text{Sn}_{1-x}\text{Pb}_x)\text{S}$ as a function of x . The closed circles indicate those obtained with the thin films, the solid lines are those of bulk $(\text{Sn}_{1-x}\text{Pb}_x)\text{S}$ taken from Ref. 3, and the open symbols are the calculation results obtained by DFT in this work. The dashed straight lines are guides for eyes.

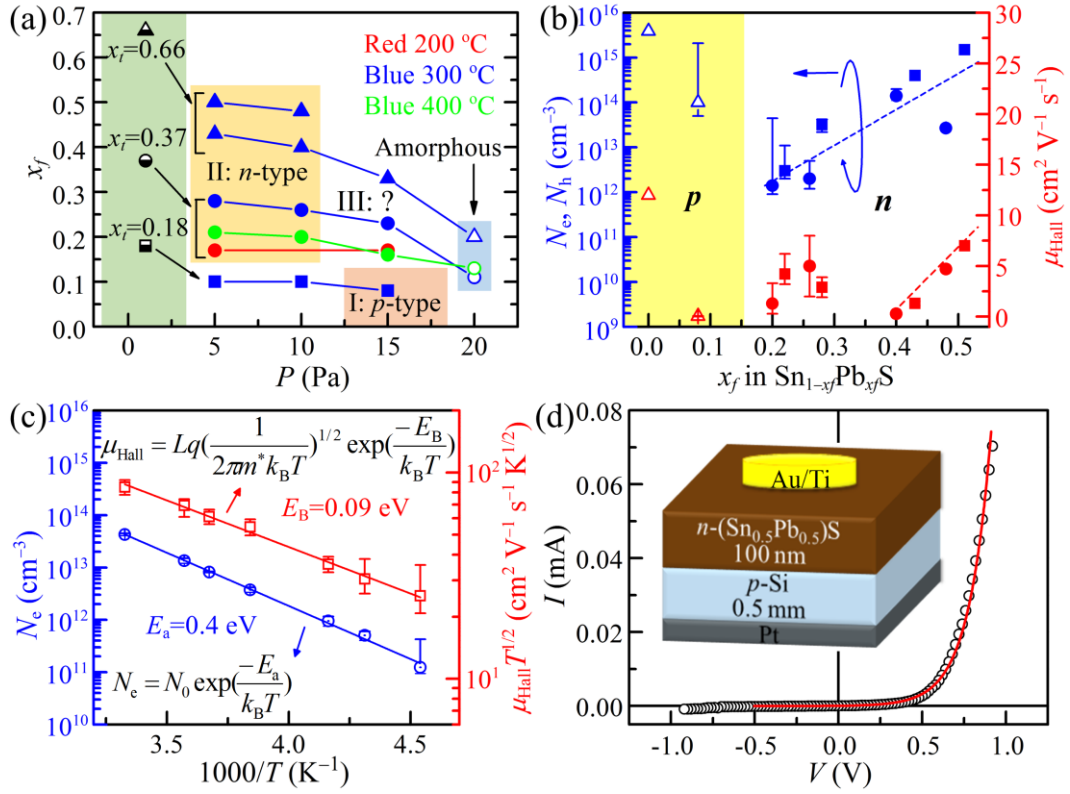


Figure 5.2. (a) Pb content in film (x_f) as a function of pressure (P), substrate temperature (T_S), and Pb content in target (x_t). The half-filled symbols indicate the targets, the closed circles the orthorhombic phase crystalline film, and the open symbols amorphous films. (b) Carrier density and mobility of $(\text{Sn}_{1-x_f}\text{Pb}_{x_f})\text{S}$ films as a function of x_f measured by Hall effect. (c) Temperature dependences of electron density (N_e , blue line) and mobility (μ_e , red line) of *n*-type $(\text{Sn}_{1-x_f}\text{Pb}_{x_f})\text{S}$ film with $x_f = 0.48$. (d) I-V characteristics of a *n*-($\text{Sn}_{0.5}\text{Pb}_{0.5}$)S/*p*-Si pn heterojunction. Inset shows the device structure.

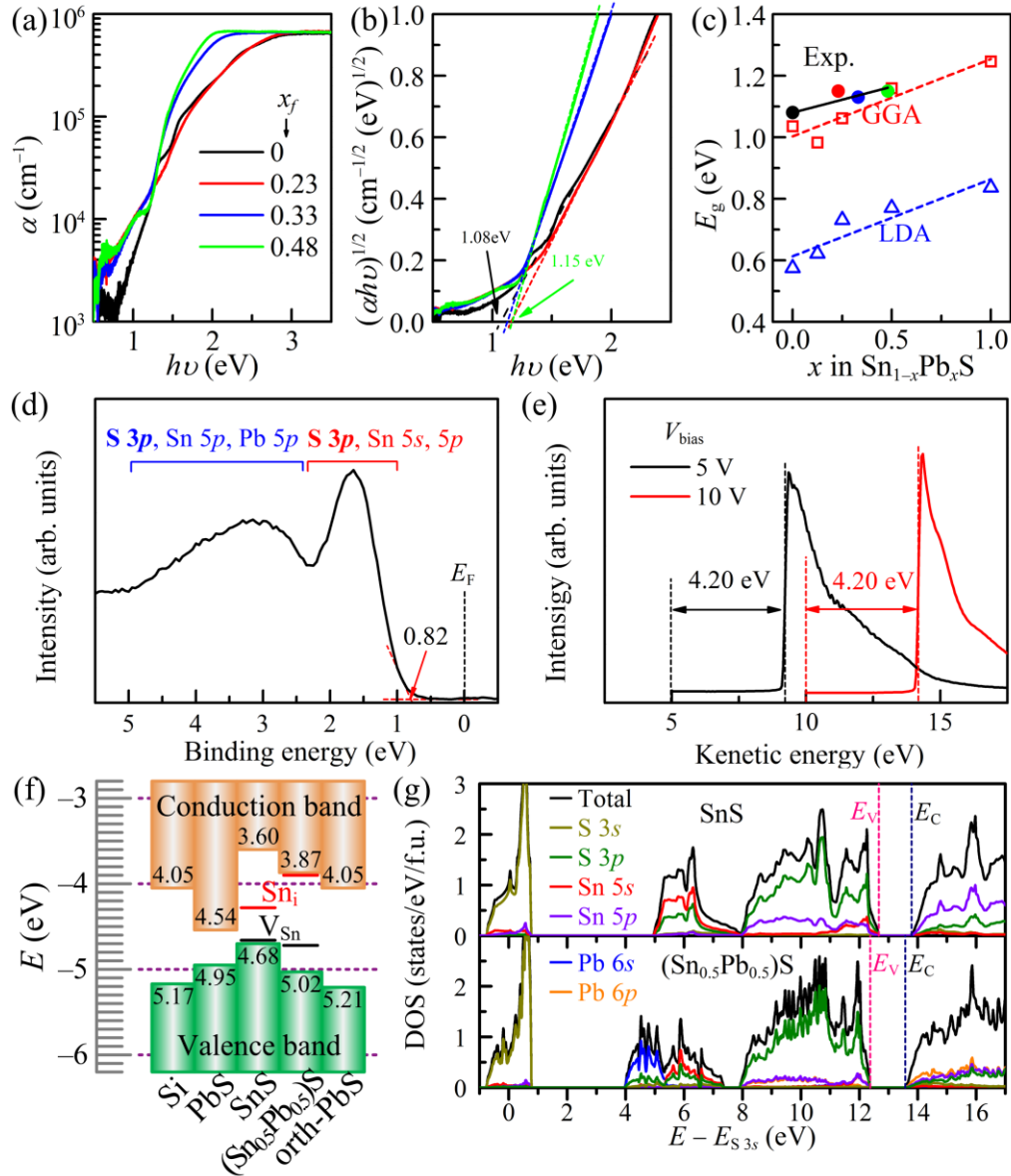


Figure 5.3. (a) Optical absorption spectra and (b) $(ah\nu)^{1/2}-h\nu$ plots of $(\text{Sn}_{1-x_f}\text{Pb}_{x_f})\text{S}$ films with various x_f . (c) Experimental and calculated bandgaps as a function of x_f . (d and e) UPS spectra of the $(\text{Sn}_{0.5}\text{Pb}_{0.5})\text{S}$ film. (f) Band alignment between Si [5], PbS [6], SnS, $(\text{Sn}_{0.5}\text{Pb}_{0.5})\text{S}$ and hypothetical orth-PbS (space group $Pnma$) (see Chapter 4). The ionization potential (IP) and electron affinity (EA) values are given in the figure. The horizontal bars indicate defect levels of Sn vacancy (V_{Sn}) and interstitial (Sn_i) in SnS and $(\text{Sn}_{0.5}\text{Pb}_{0.5})\text{S}$. (g) Total and projected densities of states (DOSs) of SnS and $(\text{Sn}_{0.5}\text{Pb}_{0.5})\text{S}$ calculated with the GGA functionals.

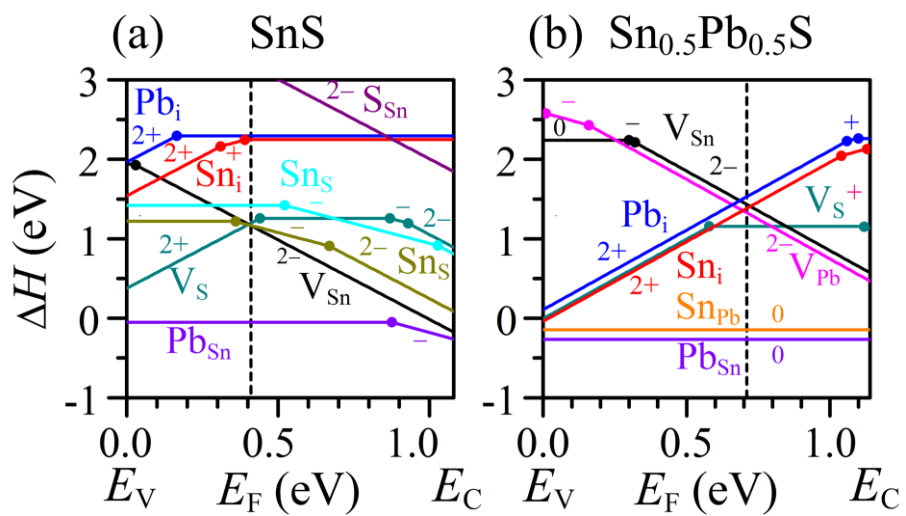


Figure 5.4. (a) Calculated formation enthalpies ΔH of intrinsic defects for (a) pure SnS and (b) $(\text{Sn}_{0.5}\text{Pb}_{0.5})\text{S}$ as a function of E_F at S-poor limit. Those of Pb impurities in SnS are also shown in (a). The values in the figures represent the charge states of the defects in the DFT calculations. The black dashed lines represent the equilibrium E_F ($E_{F,e}$) calculated self-consistently.

Chapter 6

Electronic Structure of a Perovskite Variant Cs_2SnI_6

6.1 Introduction

Lead halide perovskites invoked new development research in the third-generation photovoltaics because of the high power conversion efficiencies (PCE) of those photovoltaic cells as high as 20.1% [1–6]. These compounds are represented by the general chemical formula ABX_3 ($A = \text{Cs}$, CH_3NH_3 , or $\text{CH}_2\text{NH}=\text{CH}$; $B = \text{Pb}$ or Sn ; $X = \text{I}$, Br or Cl), where the A cations are located in the cubic network of corner-sharing $[BX_6]$ octahedra. However, these compounds and their devices suffer from the long-term instability in an ambient atmosphere, and the water-soluble toxic lead components are potential risk for the environment issue. Therefore, Sn derivatives of perovskite compounds, ASnX_3 , have been examined [7–9]. However, these ASnX_3 perovskites are very sensitive to the ambient atmosphere (oxygen, moisture, etc.) [7–11]. The instability of ASnX_3 is suggested to be related to unintentional oxidation of Sn^{2+} to Sn^{4+} , which might lead to a structural transformation and then degrade the photovoltaic performance [8,9]. Therefore, one may expect that the Sn-based perovskite compounds would be stabilized if the Sn^{4+} is employed. With this line, a class of perovskite variants A_2SnX_6 would be attractive candidates [12], because Sn in A_2SnX_6 is expected to be the 4+ oxidation state upon assumption of the A^+ and X^- oxidation states. Cs_2SnI_6 , as a typical example, has been reported to be air-stable and Cs_2SnI_6 based solar cells have exhibited promising PCEs up to 7.8% due to its intrinsic

stability and beneficial optoelectronic properties [13]. On the other hand, determination of oxidation states is not simple and easy in particular for metal cations that take multiple stable oxidation states; e.g., there have been reports on unusual oxidation states in some complex compounds such as $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ [14]. Similarly, it is not clear whether such a simple ionic $\text{Cs}^+_2\text{Sn}^{4+}\text{I}^-_6$ model is applicable for such a complex molecular iodosalts compound in which strong covalent bonds may exist.

Based on the simple ionic model, the electronic structure of Sn^{2+} -based $\text{Cs}^+\text{Sn}^{2+}\text{I}^-_3$ and Sn^{4+} -based $\text{Cs}^+_2\text{Sn}^{4+}\text{I}^-_6$ can be illustrated schematically by Figs. 6.1a and 6.1b, respectively. While the Sn 5s orbitals of $\text{Cs}^+\text{Sn}^{2+}\text{I}^-_3$ are fully-occupied [10], those of the expected $\text{Cs}^+_2\text{Sn}^{4+}\text{I}^-_6$ model are unoccupied and contribute to the conduction band minimum (CBM), similar to SnO_2 [15]. The band gaps of both $\text{Cs}^+\text{Sn}^{2+}\text{I}^-_3$ and $\text{Cs}^+_2\text{Sn}^{4+}\text{I}^-_6$ are of a charge-transfer type where the valence band maximum (VBM) and CBM are formed mainly by anions and cations, respectively.

In this chapter, the electronic structure and oxidation states of Cs_2SnI_6 were investigated by density theory functional (DFT) calculations. It is found that the VBM consists of I 5p–I 5p antibonding states, while the CBM, unexpectedly, consists of I 5p–Sn 5s antibonding states as illustrated in Fig. 6.1c. The Sn 5s orbitals indeed form electronic states ~7 eV deeper than the VBM and are fully occupied, indicating that Sn in Cs_2SnI_6 should be in the +2 oxidation state, similar to CsSnI_3 . The calculated oxidation state of I is a bit smaller than –1 and to be –2/3, because the $[\text{I}_6]$ ligand cluster is regarded to have two ligand holes and its oxidation state is $[\text{I}_6]^{4-}$ due to the I 5p–Cs 6s antibonding CBM state. The +2 oxidation state of Sn and the band gap are originated from the intracluster hybridization and stabilized by the strong covalency of the Sn–I bonds.

6.2 Computational Details

DFT calculations were performed using the projector-augmented plane wave (PAW) method implemented in the VASP code [16]. Cs ($5s$)($5p$)($6s$), Sn ($5s$)($5p$), and I ($5s$)($5p$) are treated as valence states in the PAW potentials. The plane wave cutoff energy was set to 275.4 eV. For the exchange–correlation functional, the local density approximation (LDA) and the Perdew–Burke–Ernzerhof (PBE96) [17] generalized gradient approximation (GGA) functionals underestimated the band gap for Cs_2SnI_6 (0.41 and 0.25 eV, respectively. The experimental value is 1.26 eV [13]). On the other hand, the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional [18] with the standard mixing parameter of 25% for the exact-exchange term, provided a better band gap value of 0.93 eV. In order to discuss the chemical bonding nature and the origin of the band gap more realistically, the α was adjusted to be 34 % so as to reproduce the reported band gap value, and the HSE06 with this α value will be used for the following discussion. A primitive cell containing one formula unit (f.u.) of Cs_2SnI_6 and a Γ -centered $4\times 4\times 4$ k -mesh were employed for the periodic calculations. Prior to the electronic structure calculations, variable-cell structure relaxations were performed. To reveal the origin of the band gap in Cs_2SnI_6 , calculations for hypothetical structures including $[\text{I}_6]^0$ cluster, $[\text{SnI}_6]^{2-}$ cluster, and $[\text{SnI}_6]^{2-}$ sublattice models were also performed. Additionally, chemical bonding analysis was carried out for Cs_2SnI_6 based on the crystal orbital Hamiltonian population (COHP) [19] calculated by a tight binding–linear muffin tin orbitals–atomic sphere approximation (TB-LMTO-ASA) program [20], where positive –COHP values indicate bonding states and vice versa. Integration of the –COHP spectra up to the Fermi level (E_F) yielded –ICOHP values as measure of total overlap populations (i.e., the bond order). The Bader charge analysis was carried out by the Bader program [21] with the charge density obtained by VASP.

6.3 Results and Discussion

6.3.1 Crystal and Electronic Structures of Cs_2SnI_6

Cs_2SnI_6 crystalizes into the face-centered-cubic (fcc) $\text{K}_2[\text{PtCl}_6]$ -type with the space group $Fm\bar{3}m$ (the anti-fluorite structure) and the lattice parameter a of 11.65 Å [22]. As shown in Fig. 6.2a, the unit cell is composed of four $[\text{SnI}_6]^{2-}$ octahedra at the corners and the face centers and eight Cs^{2+} cations at the tetragonal interstitials. Alternatively, Cs_2SnI_6 can be regarded as a defective variant of the perovskite CsSnI_3 , in which the $[\text{SnI}_6]$ octahedra connect to each other by sharing their corners. The Cs_2SnI_6 structure is obtained by removing a half of the Sn atoms in the CsSnI_3 structure at intervals (i.e. the edge centers and the body center in Fig. 6.2a), and thus the corner-shared $[\text{SnI}_6]^{2-}$ octahedra become isolated in Cs_2SnI_6 . After the half of the Sn atoms are removed, the $[\text{SnI}_6]^{2-}$ octahedra shrink slightly, leading to the smaller Sn–I bond length (2.85 Å [22]) in Cs_2SnI_6 than that in CsSnI_3 (3.11 Å [10]) as well as the smaller intraoctahedral I–I bond length (4.04 Å) than that of interoctahedral I–I' bond lengths (4.20 Å) (Fig. 6.2b). Table 6.1 summarizes the literature and calculated lattice parameters, bonding lengths, and band gaps. Compared with the LDA and PBE96, the HSE06 gave better results. In particular, when $\alpha = 34\%$, the HSE06 provided the lattice parameters and bonding lengths within 1.5% errors from the room-temperature experimental values and reproduced the experiment band gap value.

Figures 6.3a and 6.3b show the calculated band structure and the total and projected densities of states (DOSs) for Cs_2SnI_6 with the HSE06, respectively. The band structure of Cs_2SnI_6 exhibits a direct band gap of 1.26 eV at the Γ point. The valence band (VB) consists of I 5p orbitals, and its band width is small (only 2.38 eV in the total width). Below the VB, there is another I 5p band localized between –2.90 and –3.62 eV, which is slightly hybridized with Sn 5p orbitals. The Sn 5s orbital forms a very deep band between

-7.18 and -6.84 eV, and has little contribution to the VB. On the other hand, the conduction band (CB) extends from 1.26 to 2.56 eV and mainly consists of I 5*p* orbitals hybridized with Sn 5*s* orbitals. This breaks the above expectation in Fig. 6.1b that the CBM would consist of Sn 5*s* orbitals based on the simple ionic model of $\text{Cs}^+_2\text{Sn}^{4+}\text{I}^-_6$. Upper CB bands starts from 4.86 eV and separate from the CB with a forbidden gap of 2.30 eV, which consist of Sn 5*p*, Cs 6*s*, 5*d* and I 6*s*, 5*d* orbitals. It can also be seen that the Cs ion has little contribution to the VB and the CB.

6.3.2 Oxidation State of Sn in Cs_2SnI_6

The calculated electronic structure of Cs_2SnI_6 is represented schematically by Fig. 6.1c. Similar to the case of CsSnI_3 (Fig. 6.1a), the Sn 5*s* orbitals in Cs_2SnI_6 are occupied, which indicates that the real oxidation state of Sn in Cs_2SnI_6 is +2, similar to that in CsSnI_3 and not the expected oxidation state of +4. Based on the Sn^{2+} and the Cs^+ ions in Cs_2SnI_6 , the overall charge of the $[\text{I}_6]$ cluster must be -4 and then each I atom equivalently has an apparent fractional oxidation state of -2/3 (i.e. the $5p^{5\frac{2}{3}}$ configuration), smaller than the conventional oxidation state of -1 (i.e. the fully occupied $5p^6$ configuration); this is consistent with the above electronic structure that 1/18 of $[\text{I}_6]$ 5*p* orbitals (i.e. the single conduction band) are unoccupied. In other words, this electronic structure is understood that the $[\text{I}_6]$ ligand cluster has 2 ligand holes \underline{L}^+ and is represented as $[\text{I}^-_6\underline{L}^+]^{4-}$. This leads to converting the expected formal oxidation state of Sn^{4+} to Sn^{2+} via $\text{Sn}^{4+} \rightarrow \text{Sn}^{2+}\underline{L}^+_2$, being consistent with the calculation result.

To further support the +2 oxidation state of Sn, Bader charge analysis was performed for Cs_2SnI_6 as well as other related compounds for comparison. Figure 6.4 shows the Bader oxidation states (*Z*) of Sn calculated from the Bader charges (*N*). It should be noted that although all the *Z* values of the Sn (+1.25 and +1.56, respectively, in typical Sn^{2+} -based

compounds SnO and SnF_2 ; +2.40 and +2.71, respectively, in typical Sn^{4+} -based compounds SnO_2 and SnF_4) are underestimated, the similar values are obtained if the oxidation states are the same. The Sn in Cs_2SnI_6 has the $Z = +1.24$, close to those in SnO (+1.25), SnF_2 (+1.56), CsSnI_3 (+0.89), binary SnI_2 (+0.98), and SnI_4 (+1.16), while much smaller than those in SnO_2 (+2.40) and SnF_4 (+2.71). This result indicates that the Sn in these compounds have similar oxidation states. The similarity in the Z values between Cs_2SnI_6 and CsSnI_3 would be reasonable because the coordination structures around an Sn ion consist of $[\text{SnI}_6]$ octahedra and are similar to each other. Interestingly, the SnI_4 has the similar Z value to that in SnI_2 and other Sn^{2+} -based compounds. It implies that, unlike F, anionic I is much larger than F and other halide ions, forms more covalent bonds, and consequently its oxidation ability is not strong enough to oxidize Sn to the +4 oxidation state; SnI_4 is indeed known to be a covalent molecular compound with more covalent I–I bonds [23].

6.3.3 Bonding Nature and Origin of Band Gap in Cs_2SnI_6

The character and strength of chemical bonds were analyzed by COHP as shown in Fig. 6.3a along with the total DOS. It can be seen that the Sn–I bonds are all bonding states below E_F while antibonding ones above E_F . It should be noted that there are strong bonding states at ~ -7.4 and -3.2 eV, which originate from the strong covalent interaction between Sn $5s/5p$ and I $5p$ states. The strong covalent interaction also leads to the largest $-\text{ICOHP}$ (2.41 eV/bond) for the Sn–I bond and would be the origin of the chemical stability of Cs_2SnI_6 . In contrast, the small $-\text{ICOHP}$ value (0.10 eV/bond) for the Cs–I bond reflects the weak covalent interaction between Cs and I. On the other hand, the $-\text{COHP}$ spectra of I–I and I–I' bonds show similar patterns between -2.2 and 0 eV, where the DOS is contributed dominantly by the I $5p$ state. This pattern recalls the familiar molecular orbital (MO)

diagrams of homonuclear molecular dimers and clusters. The large antibonding states at E_F and the negative small $-\text{ICOHP}$ values (-0.24 and -0.064 eV/bond for the I–I and I–I' bonds, respectively) imply that the MOs of I $5p$ are almost filled up and no effective bond strength remains between the I ions. The bonding natures are confirmed also by the valence electron density maps on the (200) and (400) planes, as shown in Figs. 6.3b and 6.3c, respectively. It can be seen that the significant electron distribution in the Sn–I bonds clearly indicate the formation of Sn–I covalent bond. In contrast, there is little electrons between Cs–I, meaning that little covalent bond exist in the Cs–I bonds.

To understand the chemical bonding nature and the origin of the band gap in Cs_2SnI_6 , DFT calculations for some hypothetic structures were performed. First, the electronic structure for an isolated $[\text{I}_6]$ octahedron (i.e., $[\text{I}_6]^0$ cluster) was examined, as shown in Fig. 6.6a. According to the energy eigenvalues at the Γ point and the group theory, the 18 I $5p$ orbitals of the $[\text{I}_6]$ octahedra are split to 7 groups [24]. The 6 radial I $5p$ orbitals split to 3 groups of a_{1g} (I–I bonding) and e_g & t_{1u} (I–I antibonding). The 12 tangential I $5p$ orbitals form 4 triply degenerated groups of $1t_{1u}$ & t_{2g} (I–I bonding) and t_{2u} & t_{1g} (I–I antibonding). These groups are qualitatively arranged on the energy scale in Fig. 6.6d.

By adding an Sn atom and 2 electrons (transferred from the two Cs atoms, which is ionized to Cs^+ in Cs_2SnI_6) into the $[\text{I}_6]$ octahedron, the electronic structure of a $[\text{SnI}_6]^{2-}$ octahedron cluster was calculated. The resulted DOSs are shown in Fig. 6.6b and the derived energy levels are qualitatively illustrated in Fig. 6.6d. The shallow Sn $5p$ orbitals slightly hybridize with the $[\text{I}_6]$ t_{1u} orbitals, leading to Sn $5p$ – $[\text{I}_6]$ t_{1u} bonding states at -2.77 eV and Sn $5p$ – $[\text{I}_6]$ t_{1u} antibonding states at 5.45 eV. The deep Sn $5s$ orbitals strongly hybridize with the $[\text{I}_6]$ a_{1g} orbitals (see the inset to Fig. 6.6d), resulting in the Sn $5s$ – $[\text{I}_6]$ a_{1g} bonding states at -6.65 eV and the Sn $5s$ – $[\text{I}_6]$ a_{1g} antibonding states at 2.36 eV. These

results are consistent with the –COHP analysis of Sn–I (the second panel of Fig. 6.5a). The Sn $5s$ and $5p$ orbitals have little hybridization with the other 5 groups of I $5p$ orbitals (i.e. t_{2g} , t_{2u} , e_g , t_{1g} and $2t_{1u}$). Note that the $2t_{1u}$ orbitals are fully occupied while the Sn $5s$ –[I₆] a_{1g} antibonding orbital is unoccupied in the [SnI₆]^{2–} cluster, and the [SnI₆]^{2–} cluster forms a semiconductor-type electronic structure with the band gap of 2.36 eV.

Finally, a [SnI₆]^{2–} sublattice model in which [SnI₆]^{2–} are located at the corner and the face-center sites in the unit cell of Cs_2SnI_6 (i.e., the Cs^+ ions are removed from Cs_2SnI_6) was examined. The resulted DOSs (Fig. 6.6c) are very similar to that of Cs_2SnI_6 (Fig. 6.3b), indicating that Cs^+ cations have limited contribution to the electronic structure of Cs_2SnI_6 except for slightly pushing up the bands above E_F . The localized orbitals in the [SnI₆]^{2–} cluster model expand into dispersed bands made of the [SnI₆]^{2–} sublattice. The unoccupied Sn $5s$ –[I₆] a_{1g} antibonding orbitals forms the CBM, and the occupied [I₆] $5p$ (t_{2g} , t_{2u} , e_g , t_{1g} , and $2t_{1u}$) orbitals, which are antibonding between two I ions while non-bonding states to Sn, form the VBM.

6.4 Conclusions

In conclusion, the real oxidation state of Sn in Cs_2SnI_6 is +2, which is the same as that in CsSnI_3 but different from the previously-expected value +4. DFT calculations clarified that the +2 oxidation state and the band gap are formed due to the intracenter hybridization in the [SnI₆] clusters and stabilized by the strong covalent nature of the Sn–I bonds. The Sn^{2+} state and the apparently $\text{I}^{-2/3}$ state form the shortened and strengthened Sn–I chemical bonds, making the isolated [SnI₆]^{2–} similar to stable functional groups like [SO₄]^{2–}. The present result also shows the conventional ionic model is invalid for p -block metal-iodide

based perovskites in which ionic bonds and covalent bonds coexist and compete, and provides a guiding principle to design new perovskite-based photovoltaic materials.

References

- [1] Best Research-Cell Efficiencies, National Renewable Energy Laboratory, <http://www.nrel.gov/ncpv/>, November 2014.
- [2] A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, *J. Am. Chem. Soc.* **131**, 6050 (2009).
- [3] H. Zhou, Q. Chen, G. Li, S. Luo, T. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu, and Y. Yang, *Science* **345**, 542 (2014).
- [4] N. J. Jeon, J. H. Hoh, Y. C. Kim, K. S. Yang, S. Ryu, and S. I. Seok, *Nat. Mater.* **13**, 897 (2014).
- [5] J.-H. Im, I.-H. Jang, N. Pellet, M. Grätzel, and N.-G. Park, *Nat. Nanotech.* **9**, 927 (2014).
- [6] Y. Kutes, L. Ye, Y. Zhou, S. Pang, B. D. Huey, and N. P. Padture, *J. Phys. Chem. Lett.* **5**, 3335 (2014).
- [7] F. Hao, C. C. Stoumpos, D. H. Cao, R. P. H. Chang, and M. G. Kanatzidis, *Nat. Photon.* **8**, 489 (2014).
- [8] N. K. Noel, S. D. Stranks, A. Abate, C. Wehrenfennig, S. Guarnera, A.-A. Haghighirad, A. Sadhanala, G. E. Eperon, S. K. Pathak, M. B. Johnson, A. Petrozza, L. M. Herz, and H. J. Snaith, *Energy Environ. Sci.* **7**, 3061 (2014).
- [9] I. Chung, B. Lee, J. He, R. P. H. Chang, and M. G. Kanatzidis, *Nature* **485**, 486 (2012).
- [10] I. Chung, J.-H. Song, J. Im, J. Androulakis, C. D. Malliakas, H. Li, A. J. Freeman, J. T.

- Kenney, and M. G. Kanatzidis, *J. Am. Chem. Soc.* **34**, 8579 (2012).
- [11] Y. Zhou, H. F. Garces, B. S. Senturk, A. L. Ortiz, and N. P. Padture, *Mater. Lett.* **110**, 127 (2013).
- [12] M. G. Brik and I. V. Kityk, *J. Phys. Chem. Solids* **72**, 1256 (2011).
- [13] B. Lee, C. C. Stoumpos, N. Zhou, F. Hao, C. Malliakas, C.-Y. Yeh, T. J. Marks, M. G. Kanatzidis, and R. P. H. Chang, *J. Am. Chem. Soc.* **136**, 15379 (2014).
- [14] W.-T. Chen, T. Soito, N. Hayashi, M. Takano, and Y. Shimakawa, *Sci. Rep.* **2**, 449 (2012).
- [15] J. Robertson, *J. Phys. C Solid State Phys.* **12**, 4767 (1979).
- [16] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [17] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [18] J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **124**, 219906 (2006).
- [19] R. Dronskowski and P. E. Blöchl, *J. Phys. Chem.* **97**, 8617 (1993).
- [20] O. Jepsen, A. Burkhardt, and O. K. Andersen, The program TB-LMTO-ASA, Ver.4.7; Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany, 1999.
- [21] W. Tang, E. Sanville, and G. Henkelman, *Phys.: Condens. Matter.* **21**, 084204 (2009).
- [22] W. Werker, *Recl. Trav. Chim. Pays-Bas Belg.* **58**, 257 (1939).
- [23] M. Cordey-Hayes, *J. Inorg. Nucl. Chem.* **26**, 915 (1964).
- [24] G. V. Vajenine and R. Hoffmann, *J. Am. Chem. Soc.* **120**, 4200 (1998).

Table 6.1. Literature and calculated lattice parameters, bonding lengths and band gaps of Cs_2SnI_6 .

	Exp.	LDA	PBE96	HSE06 ($\alpha=25\%$)	HSE06 ($\alpha=34\%$)
a (Å)	11.65 [22]	11.26	12.03	11.86	11.82
Cs-I (Å)	4.12 [22]	3.98	4.25	4.19	4.18
Sn-I (Å)	2.85 [22]	2.83	2.91	2.89	2.88
I-I (Å)	4.04 [22]	4.00	4.11	4.09	4.07
I-I' (Å)	4.20 [22]	3.96	4.39	4.30	4.29
E_g (eV)	1.26 [13]	0.13	0.25	0.93	1.26

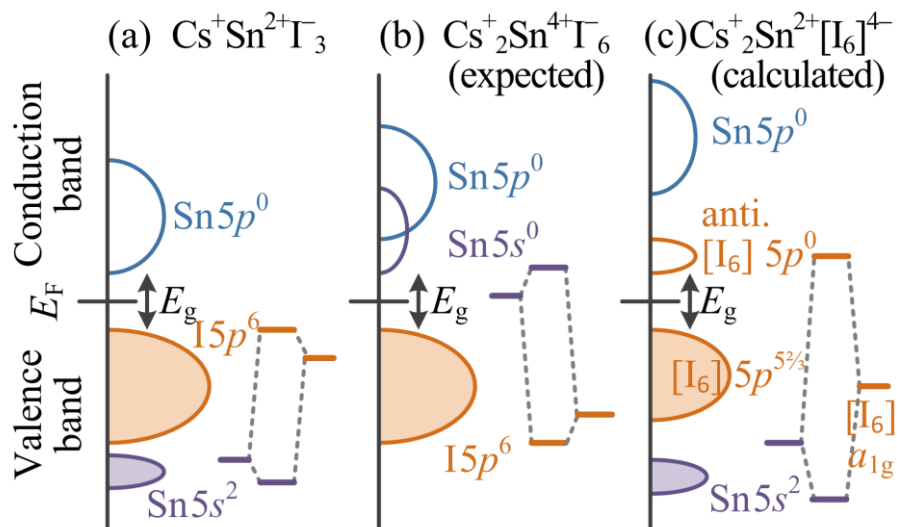


Figure 6.1. Schematic electronic structure for (a) $\text{Cs}^+\text{Sn}^{2+}\text{I}_3^-$ (b) previously-expected $\text{Cs}^+_2\text{Sn}^{4+}\text{I}_6^-$, and (c) calculated $\text{Cs}^+_2\text{Sn}^{2+}[\text{I}_6]^{4-}$. The molecular orbital energy diagrams for Sn 5s–I 5p bonds are also shown schematically on bottom-left in each figure.

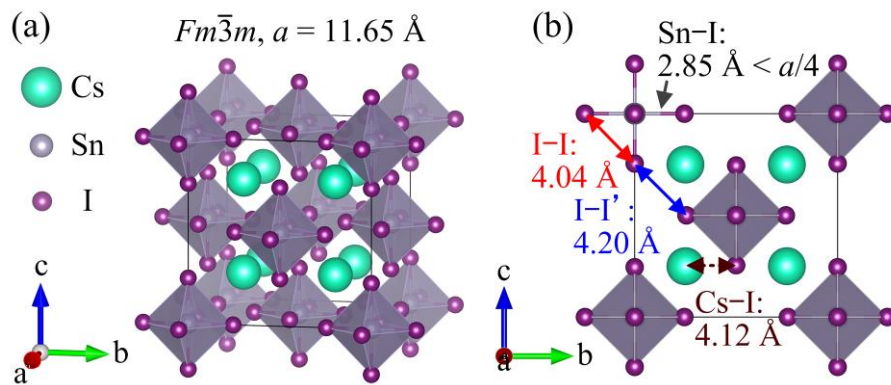


Figure. 6.2. (a) Crystal structure of Cs_2SnI_6 and (b) top view of (a). The bonding lengths from Ref. 22 are shown in (b).

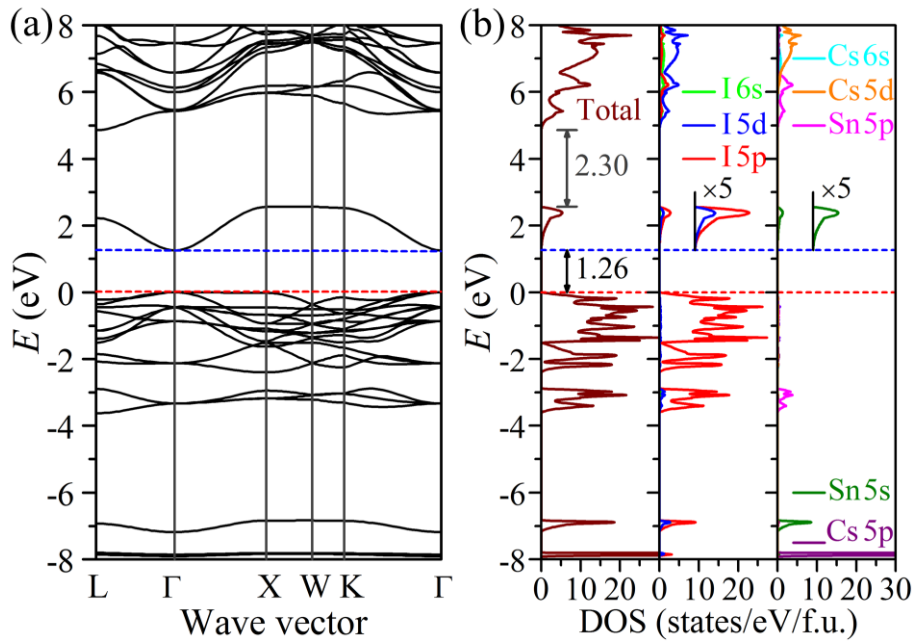


Figure 6.3. (a) Band structure and (b) total and projected DOSs of Cs_2SnI_6 calculated with HSE06. The red and blue dashed lines mark the VBM and the CBM, respectively.

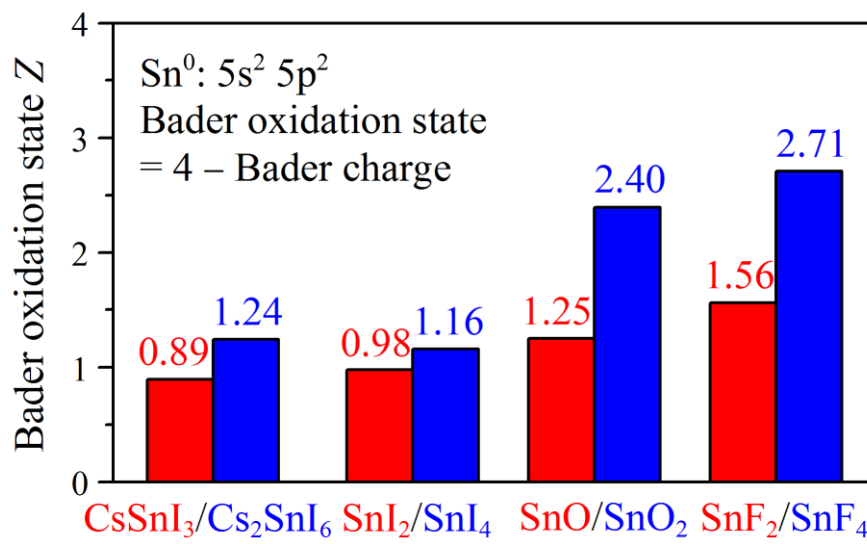


Figure. 6.4. Bader oxidation states Z of Sn in Sn-based compounds.

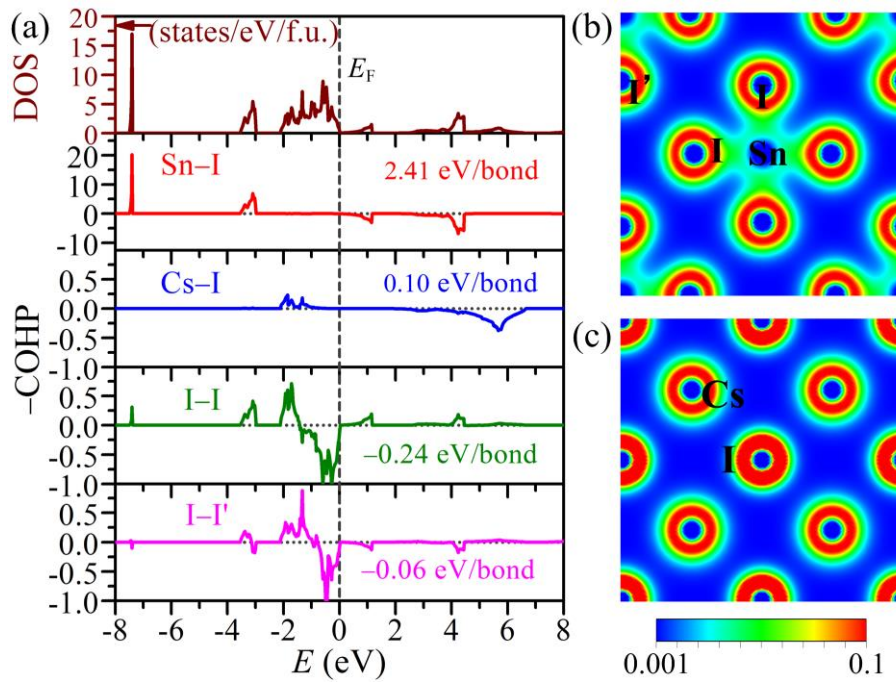


Figure 6.5. (a) Calculated $-\text{COHPs}$ for Sn-I, Cs-I, I-I, and I-I' bonds. The total DOS is shown in the top panel for comparison. The $-\text{ICOHP}$ values for Sn-I, Cs-I, I-I, and I-I' are also shown in respective panels. (b and c) Valence electron density maps on the (b) (200) and (c) (400) planes.

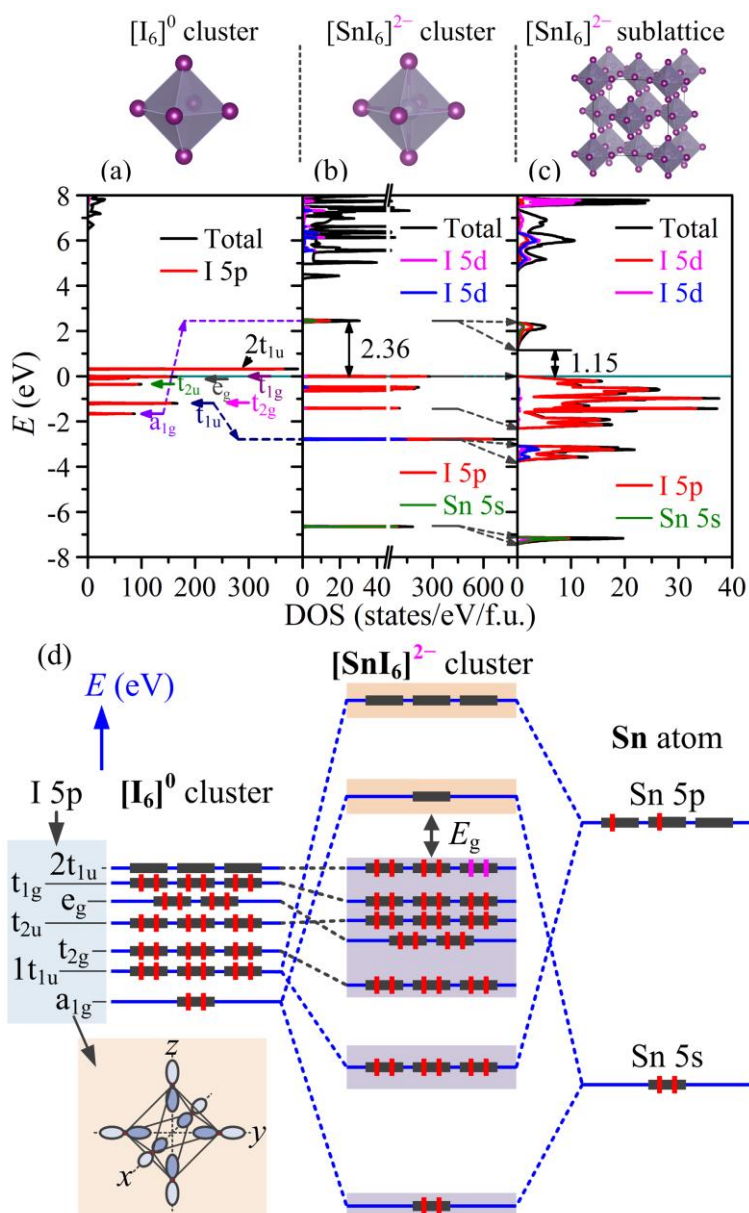


Figure 6.6. Total and projected DOSs of (a) $[\text{I}_6]^0$ cluster, (b) $[\text{SnI}_6]^{2-}$ cluster, and (c) $[\text{SnI}_6]^{2-}$ sublattice models. The structures of the $[\text{I}_6]$ cluster, the $[\text{SnI}_6]$ cluster and the $[\text{SnI}_6]$ sublattice models are shown on top. (d) Qualitative interaction diagram for the $[\text{I}_6]^0$ cluster, the $[\text{SnI}_6]$ cluster, and the $[\text{SnI}_6]$ sublattice models. The orbitals are qualitatively arranged on the energy scale. Inset of (d) shows a schematic illustration of $[\text{I}_6] a_{1u}$ orbital.

Chapter 7

Intrinsic Defects in a Perovskite Variant Cs_2SnI_6

7.1 Introduction

In Chapter 6 the density functional theory (DFT) calculations indicate that the real oxidation state of Sn in Cs_2SnI_6 is closer to +2, similar to CsSnI_3 , which originates from the nominal formula $\text{Cs}^+_2\text{Sn}^{2+}[\text{I}_6]^{4-}$. It is known well that the typical Sn^{2+} -based compounds, including SnO [1], SnS [2], and CsSnI_3 [3], in general, intrinsically exhibit good p -type conductivity because V_{Sn} in these compounds are easily formed and act as shallow acceptors to produce mobile holes. On the other hand, Cs_2SnI_6 have not shown p -type conductivity unlike the other Sn^{2+} -based compounds and have shown n -type conduction or insulating behavior depending on the synthetic routes. Lee *et al.* [4] reported the native n -type conduction with electron density (n) of $\sim 1 \times 10^{14} \text{ cm}^{-3}$ in polycrystalline Cs_2SnI_6 pellets annealed at 200 °C, while Zhang *et al.* [5] observed very high resistivity in room temperature-processed Cs_2SnI_6 . Therefore, in order to clarify the intrinsic nature of Cs_2SnI_6 and its origin, a systematic theoretical study on the intrinsic defects is important, which will provide a guiding principle for tuning its properties for photovoltaic and other semiconductor applications.

In this chapter, the formation enthalpy (ΔH) of intrinsic defects in Cs_2SnI_6 was studied by DFT calculations. It is clarified that I vacancy (V_{I}) and Sn interstitial (Sn_{I}) are mainly responsible for the intrinsic n -type conductivity in Cs_2SnI_6 . V_{Sn} , which is usually a

dominant p -type defect in Sn²⁺-based compounds, is hardly formed in Cs₂SnI₆ because of its high ΔH resulted from the low chemical potential of Sn. It is also clarified that intrinsic p -type conductivity is hardly be attained in pure Cs₂SnI₆ due to the absence of an effective acceptor with sufficiently low ΔH and a shallow transition level. The origin of deep transition levels of the dominant defects in Cs₂SnI₆ is also discussed.

7.2 Computational Details

Defect calculations were performed in the framework of DFT using the projector-augmented wave (PAW) method as implemented in the VASP code [6]. Cs (5s)(5p)(6s), Sn (5s)(5p), and I (5s)(5p) orbitals are treated as valence states in the PAW potentials. The cutoff energy for the basis set was set to 275.4 eV. A 72-atoms supercell (2×2×2 primitive cells) was used to model the intrinsic defects. Atomic positions were relaxed until all the forces on the atoms were less than 0.05 eV/Å, employing a Γ -centered 3×3×3 k -mesh and the Perdew–Burke–Ernzerhof (PBE96) [7] generalized gradient approximation (GGA) functionals. The total energies were calculated by Γ point-only calculation using the Heyd–Scuseria–Ernzerhof (HSE06) [8] hybrid functional with 34% of exact nonlocal exact exchange, which was adjusted to reproduce the experimental band gap of 1.26 eV [4].

ΔH of a defect (D) in a charge state q was calculated through the equation [9]

$$\Delta H_{D,q}(E_F, \mu) = E_{D,q} - E_H - \sum n_\alpha \mu_\alpha + q(E_F + E_V + \Delta V), \quad (7.1)$$

where $E_{D,q}$ is the total energies of the supercell with the defect D in the charge state q , and E_H that of the perfect host supercell. n_α indicates the number of α atoms added ($n_\alpha > 0$) or removed ($n_\alpha < 0$), and μ_α is the chemical potential of an α atom with respect to that of an elemental phase (μ_α^{el}) by $\mu_\alpha = \mu_\alpha^{\text{el}} + \Delta\mu_\alpha$. The chemical potentials of elemental phases $\mu_{\text{Cs}}^{\text{el}}$,

$\mu_{\text{Sn}}^{\text{el}}$, and $\mu_{\text{I}}^{\text{el}}$ are taken from elemental Cs (the cubic phase, space group $Fm-3m$) [10], β -Sn (tetragonal, space group $I4_1/amd$) [11], and I_2 (orthorhombic, space group $Cmca$) [12], respectively. E_{F} is the Fermi level relative to the valence band maximum (VBM, E_{V}), which was corrected by ΔV through electrostatic potential alignment [13]. For charged defects, the image charge correction was also applied to eliminate the supercell finite-size effects [13].

μ_{α} varies depending on the experimental condition during growth or annealing. First, to stabilize the Cs_2SnI_6 phase, the following thermodynamic equation must be satisfied

$$2\Delta\mu_{\text{Cs}} + \Delta\mu_{\text{Sn}} + 6\Delta\mu_{\text{I}} = \Delta H(\text{Cs}_2\text{SnI}_6) = -10.49 \text{ eV}, \quad (7.2)$$

where $\Delta H(\text{Cs}_2\text{SnI}_6)$ is ΔH of Cs_2SnI_6 referred to the elemental Cs, β -Sn, and I_2 . To avoid the coexistence of the Cs, the Sn, and the I_2 elemental phases, the additional conditions, $\Delta\mu_{\text{Cs}} < 0$, $\Delta\mu_{\text{Sn}} < 0$, and $\Delta\mu_{\text{I}} < 0$, are required. To exclude the secondary phases CsI (cubic, space group $Pm-3m$) [14], SnI_2 (monoclinic, space group $C2/m$) [15], SnI_4 (cubic, space group $Pa-3$) [16], and CsSnI_3 (cubic, space group $Pm-3m$) [17], the following constraints must be satisfied as well.

$$\Delta\mu_{\text{Cs}} + \Delta\mu_{\text{I}} < \Delta H(\text{CsI}) = -3.80 \text{ eV}, \quad (7.3)$$

$$\Delta\mu_{\text{Sn}} + 2\Delta\mu_{\text{I}} < \Delta H(\text{SnI}_2) = -1.69 \text{ eV}, \quad (7.4)$$

$$\Delta\mu_{\text{Sn}} + 4\Delta\mu_{\text{I}} < \Delta H(\text{SnI}_4) = -2.40 \text{ eV}, \quad (7.5)$$

$$\Delta\mu_{\text{Cs}} + \Delta\mu_{\text{Sn}} + 3\Delta\mu_{\text{I}} < \Delta H(\text{CsSnI}_3) = -5.77 \text{ eV}. \quad (7.6)$$

With all these equations satisfied, $\Delta\mu_{\text{Sn}}$ and $\Delta\mu_{\text{I}}$ (and, thus, $\Delta\mu_{\text{Cs}}$ determined from Eq 7.2) are limited to a narrow region (the yellow region in Fig. 7.1). The narrow shape indicates that the growth or annealing conditions should be carefully controlled to produce the single-phase Cs_2SnI_6 , similar to the cases of CsSnI_3 [3] and MAPbI_3 [18].

7.3 Results and Discussion

7.3.1 Properties of Intrinsic Defects in Cs_2SnI_6

I have considered intrinsic point defects in Cs_2SnI_6 including three vacancies (V_{Cs} , V_{Sn} , V_{I}), three interstitials (Cs_i , Sn_i , I_i), two cation substitutions (Cs_{Sn} , Sn_{Cs}), and four antisites (Cs_{I} , Sn_{I} , I_{Cs} , I_{Sn}). Two representative chemical potential conditions in Fig. 7.1 are chosen for the following discussion; $(\Delta\mu_{\text{Sn}}, \Delta\mu_{\text{I}})$ at A (I-rich condition) and D (I-poor) points. The calculated $\Delta H_{D,q}$ under the I-rich and I-poor conditions are plotted as a function of E_{F} in Figs. 7.2a and 7.2b, respectively. The calculated transition levels $\varepsilon(q/q')$ are plotted relative to the conduction band minimum (CBM) and valence band maximum (VBM) in Fig. 7.3. Out of the twelve intrinsic defects, four (V_{I} , Sn_i , Cs_{I} and V_{Cs}) have a sufficiently small ΔH (e.g., < 1.0 eV) to influence the electrical properties. Among them, V_{I} has the lowest ΔH (≤ 0.74 eV and ≤ 0.28 eV under I-rich and I-poor conditions, respectively) and acts as a deep donor with $\varepsilon(0/+1) = 0.74$ eV above VBM (i.e., 0.52 eV below the conduction band edge, CBM), which is mainly responsible for the n -type condition of Cs_2SnI_6 . Under the I-poor condition, Sn_i has a small ΔH (≤ 1.18 eV) and a shallower transition $\varepsilon(0/+1)$ at 0.11 eV below the CBM. Therefore, Sn_i as well as V_{I} are also dominant donors for n -type conduction. Cs_{I} is of a low ΔH but stabilized in the neutral charge state at high E_{F} (i.e. n -type conditions); therefore, it does not contribute to the n -type conduction. Only Sn_{I} is a shallow donor in Cs_2SnI_6 with the $\varepsilon(0/+2)$ above the CBM, as seen in Figs. 7.2b and 7.3. However, because of its relatively high ΔH , Sn_{I} has limited contribution to the n -type conductivity even under the I-poor condition. On the other hand, under the I-rich condition, V_{Cs} has a low ΔH (≤ 1.37 eV) and can act as a deep acceptor, but at E_{F} only above 0.51 eV from the VBM and the hole density produced is too low to compensate the electrons released by V_{I} .

The other intrinsic defects with prohibitively high ΔH are displayed by gray dashed lines in Fig. 7.2. It should be noted that V_{Sn} in Cs₂SnI₆ has high ΔH values under all the chemical potentials and is as large as 3.63 eV even under the Sn-poor condition (A point), as seen in Table 7.1. This is strikingly different from the cases of the typical Sn²⁺-based semiconductors such as SnO, SnS, and CsSnI₃, in which the ΔH values of V_{Sn} (at the VBM) are usually very small under the Sn-poor condition (i.e., 1.3 eV at E_V for SnO [1], 0.8 eV for SnS [2], and 0.3 eV for CsSnI₃ [3]). The unusually high ΔH of V_{Sn} in Cs₂SnI₆ should originate from the extremely low $\Delta\mu_{\text{Sn}}$ values in Cs₂SnI₆ (see Fig. 7.1) in comparison with CsSnI₃. For the same reason, the substitutions of Sn by Cs and I (i.e., Cs_{Sn} and I_{Sn}) also have similarly high ΔH values.

Since it is found any intrinsic defect does not work as an effective *p*-type source from the I-rich to I-poor conditions, as shown above, it would be difficult to achieve intrinsic *p*-type conduction in pure Cs₂SnI₆. Instead, Cs₂SnI₆ intrinsically exhibits *n*-type conduction due to the easy formation of V_{I} and Sn_i donors. For quantitative analysis, the equilibrium E_F ($E_{F,e}$) at room temperature were calculated by solving semiconductor statistic equations. Under the I-rich limit at the A point, $E_{F,e}$ is 0.96 eV above the VBM (see the vertical dotted line in Fig. 7.2a) and the corresponding electron density (n) is $\sim 10^{12}$ cm⁻³, which is not easily determined by a Hall effect measurement. Under the I-poor condition at the D point, $E_{F,e}$ is 1.14 eV above the VBM (see the vertical dotted line in Fig. 7.2b) and n is $\sim 10^{16}$ cm⁻³. These theoretical results seem to explain the experimental results reported to date; i.e., the electrical properties of Cs₂SnI₆ ranging from insulating [5] to low-density *n*-type conduction ($n \sim 1 \times 10^{14}$ cm⁻³) [4].

7.3.2 Origins of Deep Defect Levels in Cs₂SnI₆

The $\varepsilon(q/q')$ of the dominant defects are important in particular for solar cells because

$\varepsilon(q/q')$ in the band gap indicates that they work as an electron trap, hole trap, and/or a recombination center, which deteriorate the device performances. The dominant defects V_{Pb} in MAPbI₃ [17] and V_{Sn} in CsSnI₃ [3] have transition levels deeper than their VBMs and are inert. Also in CuInSe₂, the dominant defect V_{Cu} has an $\varepsilon(-1/0)$ at only 0.03 eV above the VBM [19]. The very shallow V_{Cu} results in good *p*-type good conduction but does not deteriorate the photovoltaic performance. In contrast, in Cs₂SnI₆, all the dominant defects (Cs_i , Sn_i , V_{I} , V_{Cs} as shown by the solid lines in Fig. 7.2) have $\varepsilon(q/q')$ in the band gap, as seen in Fig. 7.3, which would more or less hinder photovoltaic performances through short diffusion/drift length and fast recombination of photo-generated carriers, in particular when processed under the I-poor condition. These deep defects can, however, be significantly avoided by using I-rich conditions, which is located at the phase boundary between Cs₂SnI₆ and elemental I (e.g. the B point as shown in Fig. 7.2a), because their ΔH are considerably increased as seen in Table 7.1.

The defect properties as well as electronic structure of a material can qualitatively understood well based on the molecular orbital theory [17,20,21]. Here I provide a simplified interpretation for the origin of the deep nature of the intrinsic defects in Cs₂SnI₆ in comparison with representative Sn²⁺-based compounds such as SnO and CsSnI₃, by focusing on cation and anion vacancies, which generally have low ΔH and play important role on electrical properties of these compounds. Fig. 7.4a shows the calculated densities of states (DOSs) and projected DOSs (PDOSs) for SnO, CsSnI₃ and Cs₂SnI₆, where the energy is aligned by Sn 4*d* and Cs 5*s* so as to compare the energy levels. Figs. 7.4b–7.4d show the schematic energy diagrams that are derived From Fig. 7.4a. As depicted in Fig. 7.4b, the VBM of SnO consists of the antibonding states of Sn 5*s* and O 2*p* orbitals (region I in the top panel of Fig. 7.4a). For a cation vacancy V_{M} , it is known that the V_{M} transition

energy in a simple oxide is ~1 eV above VBM e.g. in ZnO [22]. Also for the SnO case, the V_{Sn} level is above the O 2*p* band (region II of the top panel of Fig. 7.4a) similar to the V_{M} in the simple oxides. As the VBM made by Sn 5*s* level is similarly high, and consequently the V_{Sn} level in SnO forms the shallow acceptor level. On the other hand, the CBM consists of antibonding Sn 5*p*–O 2*p* states and is close to the Sn 5*p* level due to the ionic character of SnO. For an oxygen vacancy V_{O} , the defect state is composed of the Sn non-bonding state, which drops slightly from the CBM [21], resulting in the shallow nature of V_{O} . Fig. 7.4c schematically illustrates the formation of the CBM, VBM, V_{Sn} , and V_{I} in CsSnI₃. Since the Cs cation does not contribute to the electronic structure around the band gap, the electronic structure of CsSnI₃ is similar to that of SnO if O is replaced with I. As a result, V_{Sn} and V_{I} in CsSnI₃ form a shallow acceptor and a shallow donor, respectively, [3] similar to those in SnO.

In contrast, Cs₂SnI₆ has a strikingly different electronic structure (see the bottom panel of Fig. 7.4a), which is schematically illustrated in Fig. 7.4d. Because the removal of the half of Sn atoms and the subsequent isolation of the [SnI₆]⁴⁻ octahedra, the energy splitting between the bonding and the antibonding states of Sn 5*s*–I 5*p* (see regions IV and I, respectively, in the bottom panel of Fig. 7.4a) become very large, and the Sn 5*s*–I 5*p* bonding energies are deepened; on the other hand, the Sn 5*s*–I 5*p* antibonding energies are pushed up and become unoccupied states, forming the CBM of Cs₂SnI₆. The VBM of Cs₂SnI₆ is composed of the I 5*p*–I 5*p* antibonding states (region II in the bottom panel of Fig. 7.4a) and is much deeper than that of CsSnI₃. This seems to explain the reported experimental observation that Cs₂SnI₆ has a deeper VBM than CsSnI₃ (–5.94 eV and –5.74 eV), respectively [5]. It should be noted that the Sn 5*s* level in Cs₂SnI₆ is deep similar to SnO and CsSnI₃ and almost fully occupied, indicating the +2 oxidation state of Sn. It is

seen that the V_{Sn} level in Cs_2SnI_6 is similar to those in SnO and CsSnI_3 , while the VBM level in Cs_2SnI_6 is far below that in CsSnI_3 ; consequently, the V_{Sn} in Cs_2SnI_6 is a deep acceptor even close to the CBM, which explains why Cs_2SnI_6 is not an intrinsic p -type semiconductor unlike CsSnI_3 .

7.4 Conclusions

In conclusion, the formation energies of intrinsic defects in the Cs_2SnI_6 perovskite variant were investigated using DFT calculations. The dominant defects are donor V_{I} and Sn_i , giving the calculated electron densities of 10^{12} – 10^{16} cm^{-3} . Unlike other Sn^{2+} -based p -type semiconductor such as SnO , SnS and CsSnI_3 , the V_{Sn} in Cs_2SnI_6 has a very high $\Delta H > 3.6$ eV and are hardly formed due to the extremely low chemical potential of Sn in Cs_2SnI_6 . The energy levels of the dominant defects are deep in the band gap and would work as recombination centers in photovoltaic applications. On the other hand, their formations would be practically suppressed by employing an I-rich synthesis condition where their densities are negligibly small due to the high ΔH . These results explain the reported experimental results and provide a clue to better understanding the unusual defect physics in p -block metal-based compounds.

References

- [1] A. Togo, F. Oba, I. Tanaka, and K. Tatsumi, *Phys. Rev. B* **74**, 195128 (2006).
- [2] Z. Xiao, F.-Y. Ran, H. Hosono, and T. Kamiya, *Appl. Phys. Lett.* **106**, 152103 (2015).
- [3] P. Xu, S. Chen, H.-J. Xiang, X.-G. Gong, and S.-H. Wei, *Chem. Mater.* **26**, 6068 (2014).
- [4] B. Lee, C. C. Stoumpos, N. Zhou, F. Hao, C. Malliakas, C.-Y. Yeh, T. J. Marks, M. G.

- Kanatzidis, and R. P. H. Chang, *J. Am. Chem. Soc.* **136**, 15379 (2014).
- [5] J. Zhang, C. Yu, L. Wang, Y. Li, Y. Ren, and K. Shum, *Sci. Rep.* **4**, 6954 (2014).
- [6] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [7] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [8] J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **118**, 8207 (2003).
- [9] C. G. Van de Walle and J. Neugebauer, *J. Appl. Phys.* **95**, 3851 (2004).
- [10] C. E. Weir, G. J. Piermarini and S. Block, *J. Chem. Phys.* **54**, 2768 (1971).
- [11] E. R. Jette and E. B. Gebert, *J. Chem. Phys.* **1**, 753 (1933).
- [12] R. M. Ibberson, O. Moze and C. Petrillo, *Mol. Phys.* **76**, 395 (1992).
- [13] S. Lany and A. Zunger, *Phys. Rev. B* **78**, 235104 (2008).
- [14] A. Smakula and J. Kalnajs, *Phys. Rev.* **99**, 1737 (1955).
- [15] R. A. Howie, W. Moser, and I. C. Trevena, *Acta Crystallogr.* **B28**, 2965 (1972).
- [16] R. G. Dickinson, *J. Am. Chem. Soc.* **45**, 958 (1923).
- [17] I. Chung, J. H. Song, J. Im, J. Androulakis, C. D. Malliakas, H. Li, A. J. Freeman, J. T. Kenney, and M. G. Kanatzidis, *J. Am. Chem. Soc.* **134**, 8579 (2012).
- [18] W.-J. Yin, T. Shi, and Y. Yan, *Appl. Phys. Lett.* **104**, 063903 (2014).
- [19] S. B. Zhang, S.-H. Wei, A. Zunger, and H. Katayama-Yoshida, *Phys. Rev. B* **57**, 9642 (1998).
- [20] W.-J. Yin, S.-H. Wei, M. M. Al-Jassim, and Y. Yan, *Appl. Phys. Lett.* **99**, (2011).
- [21] W.-J. Yin, T. Shi, and Y. Yan, *J. Phys. Chem. C* **119**, 5253 (2015).
- [22] S. J. Clark, J. Robertson, S. Lany and A. Zunger, *Phys. Rev. B* **81**, 115311 (2010).

Table 7.1. Formation enthalpies (in eV) of twelve neutral intrinsic defects in Cs₂SnI₆ at the chemical potential points A, B, C, and D shown in Fig. 7.1.

	V _{Cs}	V _{Sn}	V _I	C _{Si}	Sn _i	I _i	C _{SSn}	Sn _{Cs}	C _{Si}	Sn _I	I _{Cs}	I _{Sn}
A	1.61	3.63	0.74	2.86	2.77	2.54	3.74	3.50	1.57	5.47	2.62	1.74
B	1.37	4.11	0.74	3.10	2.28	2.54	4.46	2.78	1.81	4.98	2.38	2.23
C	1.71	5.47	0.40	2.76	0.93	2.88	5.48	1.76	1.14	3.29	3.06	3.92
D	2.07	5.47	0.28	2.40	0.93	3.00	5.12	2.12	0.65	3.17	3.54	4.04

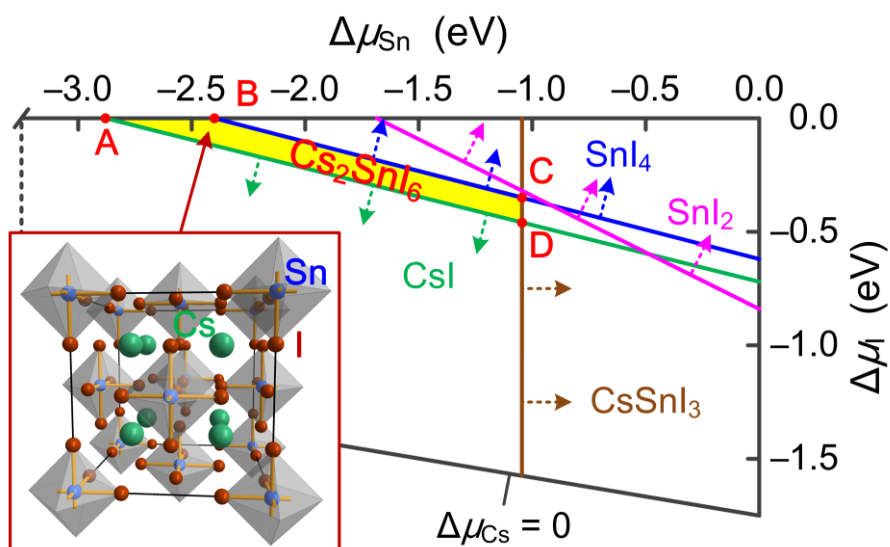


Figure 7.1. Chemical potential ($\Delta\mu_{\text{Sn}}$, $\Delta\mu_{\text{I}}$) – phase map. The yellow region A–B–C–D shows the region where Cs_2SnI_6 is stabilized against possible competitive phases including Cs, β -Sn, I_2 , CsI, SnI_2 , SnI_4 , and CsSnI_3 . The inset on left shows the crystal structure of Cs_2SnI_6 .

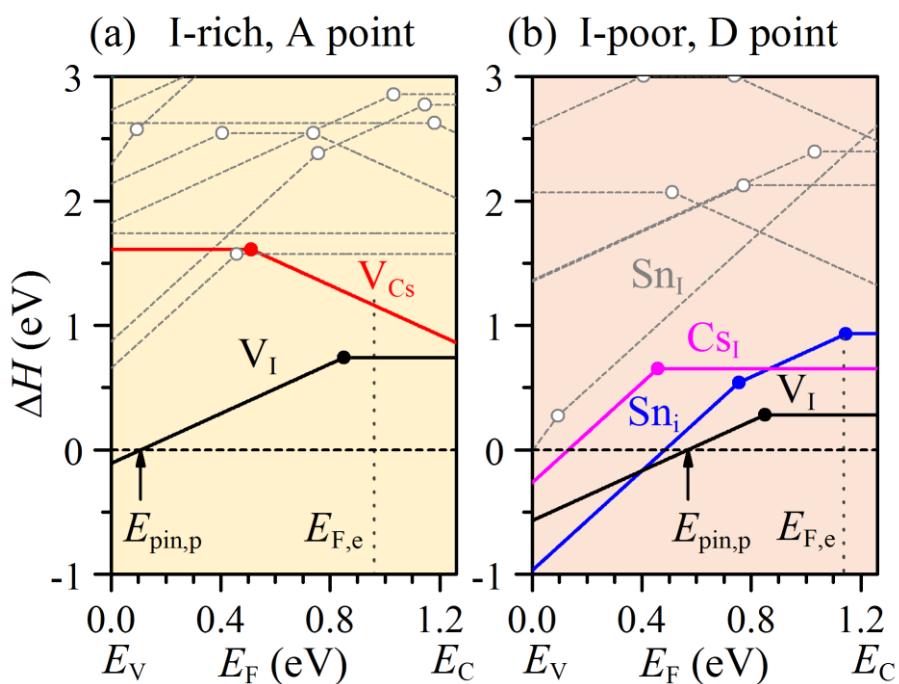


Figure 7.2. Calculated ΔH of intrinsic defects in Cs_2SnI_6 as a function of E_F at the chemical potential points in Figure 7.1, (a) A (I-rich) and (b) D (I-poor). Defects with much high ΔH values are shown by dashed lines.

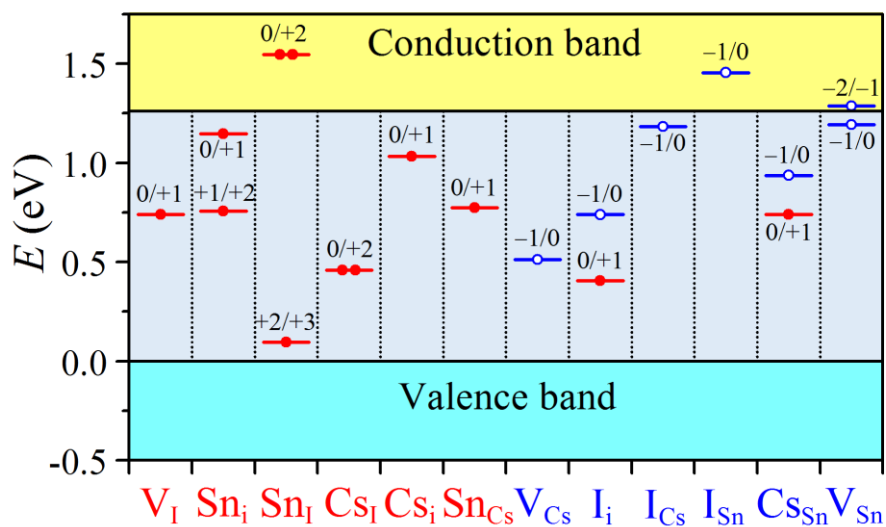


Figure 7.3. Calculated transition energy levels $\epsilon(q/q')$ for intrinsic defects in Cs_2SnI_6 . Donor and acceptor defect levels are denoted by red and blue bars, respectively. The solid and open circles at the transition levels show the number of electrons and holes that can be released during the transition of the defect charge state.

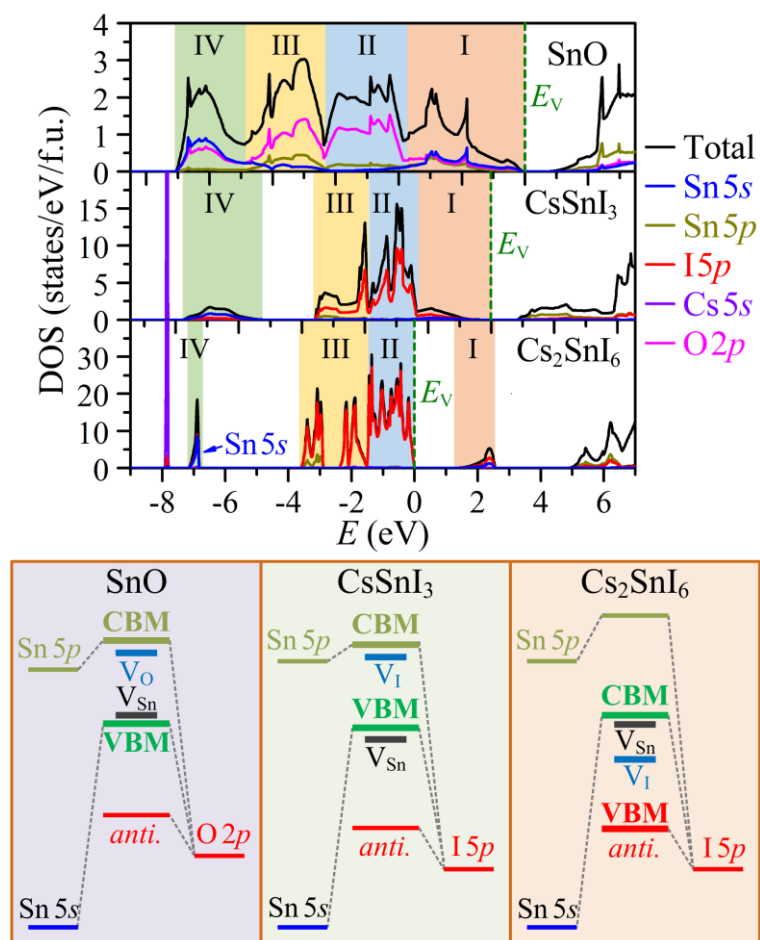


Figure 7.4. (a) Total and projected densities of states (DOSs/PDOSs) of $\text{Sn}^{2+}\text{O}^{2-}$ (top panel), $\text{Cs}^+\text{Sn}^{2+}\text{I}_3^-$ (middle panel), and $\text{Cs}_2^+\text{Sn}^{2+}[\text{I}_6]^{4-}$ (bottom panel). The energy is aligned by Sn $4d$ and Cs $5s$. (b–d) Simplified energy diagrams depicting the formation of VBM, CBM, and donor-/acceptor-like defects in (b) $\text{Sn}^{2+}\text{O}^{2-}$, (c) $\text{Cs}^+\text{Sn}^{2+}\text{I}_3^-$, and (d) $\text{Cs}_2^+\text{Sn}^{2+}[\text{I}_6]^{4-}$.

Chapter 8

General Conclusions

8.1 General Conclusions

This study was performed to develop new inorganic semiconductors with an aid of first-principles H/DFT calculations. Particular, the following two objectives are designated; one is to design *p*-type amorphous semiconductor, and the other is to clarify the origins of doping asymmetry issues in SnS and Cs₂SnI₆ and to explore new doping routes.

In [Chapter 2](#), BaZn₂As₂ was investigated for a high-mobility *p*-type semiconductor. High hole mobilities around 10 cm² V⁻¹ s⁻¹ were attained in amorphous BaZn₂As₂ thin films fabricated by pulsed laser deposition. The high mobilities should be attributed mainly to two reasons. One is the large dispersion of As 4*p* orbitals, which leads to small effective hole masses. The other is the ionic nature of As anions, which is considered to maintain the hole transport path in the amorphous structure. These results indicate that high hole mobilities would be attained even in amorphous semiconductors if heavy anions such as arsenic are employed.

In [Chapter 4](#), the origins of doping asymmetry were investigated by DFT calculations. It was revealed that the easiness of *p*-type doping and the difficulty in *n*-type doping were caused by the shallow VBM (i.e. small ionization potential) and the shallow CBM (i.e. small electron affinity), respectively. Further, it was found that the shallow VBM and CBM

are caused by the strong $s-p$ and $p-p$ couplings between Sn^{2+} cation and S^{2-} anion.

In Chapter 5, n -type conduction was realized in isovalently Pb-substituted SnS films, which are explained by two reasons. The Pb substitution deepened the VBM and CBM, and thus reduced the severity of the doping asymmetry. More importantly, the Pb substitution invoked a geometrical size effect that enlarges the interlayer distance and subsequently induces the formation of Sn and Pb cation interstitials, which result in the electron doping.

In Chapters 6 and 7, the electronic structure and the doping mechanism were studied for Cs_2SnI_6 by DFT calculations. It was found that the covalent $\text{Cs}^+_2\text{Sn}^{2+}[\text{I}_6]^{4-}$ model explains the electronic structure better than the expected ionic $\text{Cs}^+_2\text{Sn}^{2+}\text{I}^-_6$ model. It was clarified that iodine vacancy and tin interstitial are the dominant defects that are responsible for the intrinsic n -type conduction in Cs_2SnI_6 . Further, it was clarified that the doping asymmetry in Cs_2SnI_6 , i.e., the easiness of n -type doping and the difficulty in p -type doping, results from the deep CBM (i.e. large electron affinity) and the deep VBM (i.e. large ionization potential), which are formed by the unoccupied Sn $5s-I$ $5p$ antibonding states in Cs_2SnI_6 .

8.2 Future Perspective

In Chapter 2, high-mobility p -type conduction was attained by employing arsenic anions. It is expected that other heavy anions including phosphorus, antimony, tellurium and iodine would also be appropriate for designing p -type amorphous semiconductors. On the other hand, the choice of cations would also be important to control the electrical properties. In particular, it is desirable to find a new and improved semiconductors without using toxic or rare elements. Much efforts are needed to develop more p -type amorphous semiconductors,

and apply them for practical electronic devices.

In [Chapters 5](#), the geometrical doping route was proposed as a novel idea for carrier doping. This achievement proves that even keeping the same crystal structure and the ion charges, easiness of impurity doping can be altered by modifying the geometrical lattice parameters, which makes the geometrical doping route more flexible and applicable to materials in which aliovalent ion doping is not effective. On the other hand, applicability of the geometrical effect would be limited e.g. by the constituent elements and the crystal structure of a host material; therefore, it is still an important issue to find new doping routes to develop new semiconductors; e.g., it may be achieved by converting existing insulating materials into semiconductors and by solving doping asymmetry in unipolar dopable semiconductors.

Acknowledgements

The present study was carried out under the supervision of Professor Toshio Kamiya, Professor Hideo Hosono, Associate Professor Hidenori Hiramatsu, and Associate Professor Tomofumi Tada at Tokyo Institute of Technology (Tokyo Tech) from October 2012 to September 2015.

First of all, I would like to express my deepest gratitude to Professor Toshio Kamiya for all he has done for me. Prior to my doctoral course, he accepted me as an exchange student to study in his laboratory via the YSEP program from September 2011 to July 2012. Over the years, he has given me a lot of scientific suggestions and patiently guided me to first-principles calculations. Besides, he has offered me many chances to communicate with academic colleges in group meetings and academic conferences. He has also helped me a lot to get financial supports and to find a postdoctoral position. I have really enjoyed my doctoral course and learned a lot with his guidance.

I would like to express my earnest gratitude to Professor Hideo Hosono for his kind guidance and insight. He has given me many valuable comments and suggestions to improve the journal papers and this thesis. I would like also to express my gratitude to Associate Professor Hidenori Hiramatsu for his experimental help and to Associate Professor Tomofumi Tada for his valuable discussion on first-principle calculations.

I would like to express my grateful thanks to Professor Masaki Azuma, Professor Fumiyasu Oba, and Associate Professor Takao Sasagawa at Tokyo Institute of Technology for their critical referring of this thesis and valuable comments.

I would like to thank Mr. Kataya Miyase (my tutor during the YSEP program), Associate Professor Satoru Matsuishi, Dr. Yoshitake Toda, Associate Professor Hiroshi

Mizoguchi, Mr. Keisuke Ide, Dr. Kay Domen, Dr. Katsumi Abe, Mr. Hikaru Satoru, Mr. Joonho Bang, Mr. Junghwan Kim, and other laboratory members for their kindly help with experimental characterizations and measurements. I would like also to thank the project managers Professor Satoru Fujitsu and Professor Hideya Kumomi, and the laboratory secretaries Ms. Kanako Ochiai, Ms. Mayumi Nakano, and Ms. Hanae Murayama for their administrative supports.

I would like to express my deep gratitude to my cooperators and good friends Dr. Fan-Yong Ran, Dr. Hechang Lei (currently at Renmin University of China), Dr. Yanpeng Qi (currently at Max Planck Institute for Chemical Physics of Solids), Dr. Jiangang Guo (currently at Rice University), Dr. Xiao Zhang, Dr. Min Liao, Dr. Yaoqing Zhang and Mr. Yuanyuan Zhou (a PhD candidate at Brown University) not only for their active experimental corporation and valuable scientific discussion, but also for their kindly help in daily life.

Last but not least, I owe a great deal of gratitude to all my family members. My wife Yan Zeng has been my soul mate since high school. She has helped me to make many important choices and been always encouraging and urging me to do better. She has done much to take care of our family and to look after our lovely one-year-old daughter Huizhen Xiao, whose birth has inspired me so much. My parents and parents-in-law have always been understanding and supporting mine and my wife's choices. All these have made me concentrate much more on my doctoral course.

Publication List

Papers Included in the Thesis

1. “Narrow bandgap in β -BaZn₂As₂ and its chemical origins”
Zewen Xiao, Hidenori Hiramatsu, Shigenori Ueda, Yoshitake Toda, Fan-Yong Ran, Jiangang Guo, Hechang Lei, Satoru Matsuishi, Hideo Hosono, and Toshio Kamiya
Journal of American Chemical Society **136**, 14959–14965 (2014).
2. “Intrinsic defects in photovoltaic perovskite variant Cs₂SnI₆”
Zewen Xiao, Yuanyuan Zhou, Hideo Hosono, and Toshio Kamiya
Physical Chemistry Chemical Physics, **17**, 18900–18903 (2015).
3. “Route to n-type doping in SnS”
Zewen Xiao, Fan-Yong Ran, Hideo Hosono, and Toshio Kamiya
Applied Physics Letters **106**, 152103 (2015).
4. “Ligand-hole in SnI₆ unit and origin of band gap in photovoltaic perovskite variant Cs₂SnI₆”
Zewen Xiao, Hechang Lei, Xiao Zhang, Yuanyuan Zhou, Hideo Hosono, and Toshio Kamiya
Bulletin of the Chemical Society of Japan doi:10.1246/bcsj.20150110 (2015).
5. “Epitaxial growth and electronic structure of a layered zinc pnictide semiconductor, β -BaZn₂As₂”
Zewen Xiao, Fan-Yong Ran, Hidenori Hiramatsu, Satoru Matsuishi, Hideo Hosono, and Toshio Kamiya
Thin Solid Films **559**, 100–104 (2014).
6. “n-type conversion of SnS by isovalent ion substitution: Geometrical doping as a new doping route”
Fan-Yong Ran, Zewen Xiao, Yoshitake Toda, Hidenori Hiramatsu, Hideo Hosono, and Toshio Kamiya
Scientific Reports **5**, 10428 (2015).
7. “High-mobility p-type amorphous semiconductor BaZn₂As₂” (in preparation)
Zewen Xiao, Fan-Yong Ran, Min Liao, Shigenori Ueda, Hidenori Hiramatsu, Hosono Hideo, and Toshio Kamiya

Other Papers

1. “Two-dimensional transition metal electrider Y_2C ”
Xiao Zhang, * **Zewen Xiao**, * Hechang Lei, Yoshitake Toda, Satoru Matsuishi, Toshio Kamiya, and Hideo Hosono
Chemistry of Materials **26**, 6638–6643 (2014). (* shared first authors)
2. “Apparent high mobility ~ 30 cm²/Vs of amorphous In–Ga–Zn–O thin-film transistor and its origin”
Zewen Xiao, Kay Domen, Toshio Kamiya, and Hideo Hosono
Journal of the Ceramic Society of Japan **121**, 295–198 (2013).
3. “Growth of high-quality SnS epitaxial films by H₂S flow pulsed laser deposition”
Fan-Yong Ran, **Zewen Xiao**, Hidenori Hiramatsu, Hideo Hosono, and Toshio Kamiya
Applied Physics Letters **104**, 072106 (2014).
4. “Superconductivity in noncentrosymmetric ternary equiatomic pnictides LaMP ($M = Ir$ and Rh; $P = P$ and As)”
Yanpeng Qi, Jiangang Guo, Hechang Lei, **Zewen Xiao**, Toshio Kamiya, Hideo Hosono
Physical Review B **89**, 204517 (2014).
5. “Effects of Pb doping on hole transport properties and thin-film transistor characteristics of SnO thin films”
Min Liao, **Zewen Xiao**, Fan-Yong Ran, Hideya Kumomi, Toshio Kamiya, and Hideo Hosono
ECS Journal of Solid State Science and Technology **4**, Q26–Q30 (2015).
6. “Difficulty of carrier generation in PbO in comparison with SnO”
Min Liao, Seiji Takemoto, **Zewen Xiao**, Yoshitake Toda, Tomofumi Tada, Toshio Kamiya, and Hideo Hosono
to be submitted.
7. “Electron confinement in channel spaces for one-dimensional electrider”
Yaoqing Zhang, * **Zewen Xiao**, * Toshio Kamiya, and Hideo Hosono
to be submitted. (* shared first authors)

Presentation List

International Oral Presentations

1. “Unexpected electronic structure of air-stable lead-free perovskite variant Cs₂SnI₆ for photovoltaic application”
Zewen Xiao, Hechang Lei, Hidenori Hiramatsu, Hideo Hosono, and Toshio Kamiya
The 2015 MRS Spring Meeting & Exhibit, San Francisco, April 6–10, 2015.

International Poster Presentations

1. “Carrier transport and origins of narrow bandgap for *p*-type layered semiconductor, β -BaZn₂As₂”
Zewen Xiao, Fan-Yong Ran, Hidenori Hiramatsu, Hideo Hosono, and Toshio Kamiya
The 2014 E-MRS Spring Meeting and Exhibit, Lille, May 26–30, 2014.
2. “*n*-type conduction in SnS-based thin films”
Fan-Yong Ran, **Zewen Xiao**, Hidenori Hiramatsu, Hideo Hosono, and Toshio Kamiya
The 2014 E-MRS Spring Meeting and Exhibit, Lille, May 26–30, 2014.
3. “Electronic structures of Zn–Pn (*Pn* = P, As, Sb)-based layered crystals”
Zewen Xiao, Toshio Kamiya, Hiramatsu, and Hideo Hosono
The 12th Asia Pacific Physics Conference, Chiba, July 14–19, 2013.
4. “Synthesis and epitaxial growth of novel layered zinc pnictide semiconductor, β -BaZn₂As₂.”
Zewen Xiao, Hidenori Hiramatsu, Hideo Hosono, and Toshio Kamiya
The 8th International Symposium on Transparent Oxide and Related Materials for Electronics and Optics, Tokyo, May 13–15, 2013.
5. “Apparent high mobility ~ 30 cm²/Vs of amorphous In–Ga–Zn–O thin-film transistor and its origin”
Zewen Xiao, Kenji Nomura, Toshio Kamiya, and Hideo Hosono
The 6th International Conference on the Science and Technology for Advanced Ceramics, Yokohama, June 26–28, 2012.

Demotic Poster Presentations

1. “*n*-type doping in SnS: Origin of difficulty and the success by isovalent Pb-doping”
Zewen Xiao, Fan-Yong Ran, Hidenori Hiramatsu, Hideo Hosono, and Toshio Kamiya
The 11th Thin Film Materials & Devices Meeting, Kyoto, Oct 31–Nov 1, 2014.
2. “Carrier transport and origins of narrow bandgap for *p*-type layered semiconductor, β -BaZn₂As₂”
Zewen Xiao, Hidenori Hiramatsu, Hideo Hosono, Toshio Kamiya, Shigenori Ueda, and Naoki Ohashi
The 61st JSPS Spring Meeting, Sagamihara, Mar 17–20, 2014.
3. “Carrier transport of layered *p*-type semiconductor, β -BaZn₂As₂, and origins of its narrow bandgap”
Zewen Xiao, Fan-Yong Ran, Haochun Tang, Hidenori Hiramatsu, Hideo Hosono, and Toshio Kamiya
The 10th Thin Film Materials & Devices Meeting, Kyoto, Dec 31–Nov 2, 2014.
4. “Apparent high Mobility ~ 30 cm²/Vs of amorphous In–Ga–Zn–O thin-film transistors and its origin”
Zewen Xiao, Junghwan Kim, Toshio Kamiya and Hideo Hosono
The 9th Thin Film Materials & Devices Meeting, Nara, Nov 2–3, 2014.