

論文 / 著書情報
Article / Book Information

題目(和文)	前周期遷移金属を用いた新規半導体の設計
Title(English)	Design for Novel Semiconductors Based on Early Transition Metals
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

論文要旨

THESIS SUMMARY

専攻 : Department of	材料物理科学	専攻	申請学位 (専攻分野) : Academic Degree Requested	博士 (工学) Doctor of
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要旨 (英文 800 語程度)
Thesis Summary (approx.800 English Words)

Wide bandgap semiconductors are in demand for applications in power electronics and optoelectronics. However, control of carrier polarity, which is required for the realization of bipolar semiconductors, has been a major challenge for wide gap semiconductors. Conventionally, these semiconductors have been studied with compounds of post transition metal (*p*TM) cations because the large spherical spread of unoccupied *s* orbitals in *p*TM cations realizes the high efficient *n*-type conductivity. However, their compounds have often exhibited instability to carrier doping owing to their multiple stable valence states.

This doctoral thesis provides the design for wide bandgap semiconductors based on early transition metal (*e*TM) cations, which have not attracted much attention so far. Contrary to the *p*TM cations, the *e*TM cations such as Y^{3+} and Zr^{4+} have the high and stable valence state, being expected to provide the high controllability of carrier polarity when impurity doping. In addition, since the *e*TM cations form a stable double anionic compound, the electronic structure suitable for the desired functionality can be obtained by choosing the anions.

In the present study, the compositions, AChX (A = Y, Zr, La, and Hf, Ch = chalcogens, and X = oxygen and fluorine), were focused because X anion widens the bandgap due to its high Madelung potential and chalcogen anion is suitable for *p*-type conduction owing to its small ionization potential and spatially spread *p* orbitals. In addition, the electronic structure appropriate for bipolarity was designed by choosing crystal structure.

Chapter 1 summarizes the previous research related to design for semiconductor and the theory of chemical bonding and defect physics in semiconductors. In addition, the strategy and purpose of the present study are described.

Chapter 2 presents the design guideline for choosing the crystal structure suitable for transparent bipolar semiconductors. Tetragonal ZrOS (*t*-ZrOS), whose structure type is PbClF, was chosen as the candidate according to the following three guidelines. (1) In order to realize *n*-type conductivity, non-bonding state between Zr $4d_{x^2-y^2}$ and S/O *p* orbitals is utilized to make the conduction band minimum (CBM) level deep. (2) Strong anti-bonding nature from short separation between sulfur leads to shallow valence band maximum (VBM) level suitable for the hole transport. (3) The forbidden optical transition between VBM and CBM states ensures optical transparency in visible light. As results of the experiment, *t*-ZrOS exhibited *n*- and *p*-type transport by substituting F on the S site and Y on the Zr site,

respectively. The electrical conductivity at 300 K was $\sim 10^{-7}$ S/cm in undoped sample and $\sim 10^{-2}$ S/cm in doped samples with both carrier types. In addition, the Fermi level shift 1.4 eV between *n*- and *p*-type samples was observed by hard x-ray photoemission spectroscopy (HAXPES). This result was consistent with the bandgap which is 1.5 eV detected by diffuse reflection measurement. Finally, the band alignment was revealed with ultraviolet photoelectron spectroscopy and HAXPES. The VBM and the CBM of t-ZrOS were valid energy levels for the emergence of bipolarity, demonstrating the validity of the design. In addition, since the cubic phase of ZrOS indicated small electron affinity and large ionization potential, it was concluded that selection of the crystal structure largely affected the band alignment.

In chapter 3, hexagonal LaSeF (*h*-LaSeF) was introduced as the candidate of wide-gap bipolar semiconductor. As the material design, Se anion is useful for *p*-type owing to its small ionization potential and F anion widens bandgap due to its high Madelung potential. In addition, La cation prevents the formation of killer defect generating the hole carrier because of its stable valence state and high coordination number, resulting in the efficient electron dopability. The CBM and VBM states of *h*-LaSeF are composed of the bonding between La $5d_{z^2}$ and the anti-bonding between Se $4p_z$, respectively. Those band edge states consist of non-bonding between cation and anion, resulting in the small effective masses of hole and electron. For the validation of material design, the impurity substitution was done to obtain bipolar doping. Substituting Ca into La induced the hole transport in *h*-LaSeF. On the other hand, Cl 1% doping on Se site stabilized tetragonal phase of LaSeF (*t*-LaSeF) and simultaneously converted to *n*-type conductivity. The electrical conductivity was $\sim 10^{-9}$ S/cm in the undoped sample and $\sim 10^{-1}$ S/cm in the doped sample. Furthermore, the bandgap values were detected as ~ 2.9 eV in *h*-LaSeF and ~ 2.2 eV in *t*-LaSeF by using the diffuse reflection measurement. These results indicated the good controllability of carrier density and polarity in the wide-gap semiconductor.

Chapter 4 is the general conclusion of the present study. In conclusion, the *e*TM based semiconductors will be the platform of widegap semiconductors by choosing the appropriate crystal structure and anions.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note: Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).

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(博士課程)

Doctoral Program

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