

論文 / 著書情報
Article / Book Information

題目(和文)	太陽光エネルギー変換応用を目的とした3元系亜鉛窒化物半導体の理論的研究
Title(English)	Theoretical Study of Ternary Zinc Nitride Semiconductors for Solar Energy Conversion
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出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第12094号, 授与年月日:2021年9月24日, 学位の種別:課程博士, 審査員:神谷 利夫,大場 史康,平松 秀典,熊谷 悠,山本 隆文
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第12094号, Conferred date:2021/9/24, Degree Type:Course doctor, Examiner:,,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

論文要旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	材料 材料	系 コース	申請学位 (専攻分野)： 博士 Academic Degree Requested Doctor of	(工学)
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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

Solar energy is immensely attractive as a renewable energy source because of its abundance and the imminent exhaustion of fossil fuels. Solar cells are key devices for utilizing solar energy. Although various photoabsorber materials have been developed in the past several decades, photoabsorbers that achieve high power conversion efficiencies typically contain precious metals or toxic elements such as III-V compounds, Cu(In,Ga)(S,Se)₂, CdTe, and lead halide perovskites. Of the alternative photoabsorber materials thus far reported, ternary zinc nitrides are of particular interest because they can be manufactured entirely from earth-abundant and non-toxic elements and have suitable electrical and optical properties. The design and exploration of ternary zinc nitrides based on first-principles calculations have been accelerating in recent years, and previously unreported materials such as CaZn₂N₂ have been proposed theoretically and verified experimentally. However, unexplored chemical space of the ternary zinc nitrides remains. Further investigations are expected to identify more promising materials.

In this thesis, I focused on AZn₂N₂-type and AZn₃N₃-type ternary zinc nitrides and their crystal structures were determined using computational screenings based on first-principles calculations. In addition, I theoretically investigated their fundamental electronic and point-defect properties and experimentally verified the predicted crystal and electronic structures. The major results obtained in this study are as follows.

My computational screening for the crystal structures of AZn₂N₂ revealed that SrZn₂N₂ is stable whereas BaZn₂N₂ is metastable. SrZn₂N₂ takes an anti-La₂O₃-type crystal structure, which is the same as the crystal structure of CaZn₂N₂. My calculations showed that SrZn₂N₂ has a direct-type band structure with low electron and hole effective masses and shows strong optical absorption. Theoretical defect analysis indicates that the N vacancy generates defect levels at 0.19 and 0.44 eV above the valence band maximum. However, the N vacancy is unlikely to significantly affect the photovoltaic performance when the Fermi level is positioned at the mid-gap or *n*-type region by optimization of crystal growth conditions or extrinsic doping. The SrZn₂N₂ powder was synthesized by NH₃ nitridation of SrZn₂ alloy at 600°C. The band gap of SrZn₂N₂ was experimentally determined to be 1.6 eV, which is close to the theoretical value. SrZn₂N₂ is a promising material for single-junction solar cells because it has an optimal band gap and electrically benign point-defect properties and consists of earth-abundant elements.

Additionally, a systematic comparison of CaZn₂N₂, SrZn₂N₂, and CaMg₂N₂ was conducted. My integrated approach with chemical bonding analysis and defect energetics showed that, in CaZn₂N₂ and SrZn₂N₂, the Zn-3*d* states construct antibonding interactions with the N-2*p* states and push up the valence band maxima, resulting that the localized states induced by the cation vacancies are located near or in the valence bands. In contrast, the cation vacancies in CaMg₂N₂ generate deep defect levels due to no antibonding interaction near the valence band maximum. Among the ternary zinc nitrides, the defect levels of the Zn vacancy in CaZn₂N₂ are shallower than in SrZn₂N₂ because of the stronger antibonding interaction of the Zn-3*d* and N-2*p* states.

I also explored the crystal structures of previously unreported ScZn₃N₃ and YZn₃N₃. The predicted ground-state structures of ScZn₃N₃ and YZn₃N₃ are the ScAl₃C₃-type. The YZn₃N₃ phase is more stable than its competing phases while the ScZn₃N₃ phase is metastable. My calculations revealed that YZn₃N₃ has a direct-type band structure with a band gap of 1.8 eV and that its native defects are unlikely to make a significant impact on carrier lifetime thanks to the antibonding interaction of the Zn-3*d* and N-2*p* states as well as CaZn₂N₂ and SrZn₂N₂. I also grew YZn₃N₃ films on glass substrates by reactive co-sputtering and validated the theoretically predicted crystal structure. The experimentally determined band gap of 1.8 eV agrees well with the theoretical value. Given its appropriate band gap, low effective masses, high optical absorption, and good defect behavior, I propose YZn₃N₃ as a new candidate for top-cell materials in tandem solar cells.

The ternary zinc nitrides SrZn₂N₂ and YZn₃N₃ identified in this study are attractive candidates for solar absorbers. These materials are found to show strong optical absorption associated with their direct-type band structures and have optimal band gaps for single-cell and top-cell photoabsorbers, respectively. My theoretical calculations have also elucidated that the valence band maxima of SrZn₂N₂ and YZn₃N₃ include the antibonding interactions of the Zn-3*d* and N-2*p* states and the defect-induced acceptor levels in these materials tend to be shallow or buried in the valence bands thanks to the antibonding interactions. This defect behavior is suited to the active layers for solar energy conversion.

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 1copy of 800 Words (English).

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