論文 / 著書情報
Article / Book Information

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種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
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論 文 要 旨

THESIS SUMMARY

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

Wide-gap semiconductors have a number of applications in power devices, transparent electrodes, light-emitting diodes, and so on. The performance of these devices is closely associated with not only the electronic states in the valence bands (VBs) and conduction bands (CBs) of the host materials but also defect-induced states. Oxides are attractive for such applications owing to their good atmospheric stability, ease of synthesis, and low material cost. While the prime constituents of the CBs of typical oxide semiconductors (Ga_2O_3, In_2O_3, ZnO, TiO_2, etc.) vary depending on the cation species, their VBs are mainly composed of the O 2*p*-orbitals, whose deep and localized nature could lead to high ionization potential and hole effective masses. This feature explains that *p*-type oxide semiconductors are considerably rarer than *n*-type ones.

In terms of defect formation, the following three conditions need to satisfy to achieve high *p*-type conductivity: (i) self-trapped holes (STHs) are unstable, (ii) hole compensation by donor-type native defects does not significantly occur, and (iii) a shallow acceptor with a low formation energy exists. To my knowledge, no oxides whose valence band maximum (VBM) consists of O 2*p*-orbitals satisfy all of these conditions. From this circumstance, the direction of pioneering wide-gap *p*-type semiconductors has shifted from pure oxides in which O 2*p*-orbitals form the VBM to oxides containing cations with s^2 or d^{10} electronic configurations and oxychalcogenides.

In this thesis, I mainly focus on systems in which the VBM is not predominantly made up of O 2*p*-orbitals. Specifically, the properties of point defects in several wide-gap oxides and non-Cu-based oxychalcogenides are investigated using first-principles calculations. The series of studies aim to obtain design concepts for wide-gap *p*-type semiconductors and propose promising materials.

I performed exhaustive calculations of the STHs and O vacancies in nine prototypical binary oxides (Al_2O_3, Ga_2O_3, In_2O_3, TiO_2, ZrO_2, HfO_2, Sc_2O_3, Y_2O_3, and ZnO) to grasp the trends regarding the stability of these defects. The STH stability and the formation energy of O vacancies can classify the nine oxides into ZnO with significant cation orbital hybridization and the others. In the former, the STHs are not stabilized, and the formation energy of O vacancies is positive throughout the entire Fermi level range within the band gap. In contrast, the STHs are stable, and the formation energies of O vacancies are negative when the Fermi level is low in the latter. Thus, not only STH stabilization but also hole compensation by O vacancies is a factor that hinders *p*-type doping of the eight oxides other than ZnO. This undesired defect formation could be suppressed by selecting a system in which other orbitals contribute to the VBM, as in the case of ZnO.

I investigated the behavior of point defects in $CuMO_2$ (*M* = Al, Ga, In), a well-known Cu-based *p*-type semiconductor, to obtain insights into the origin of *p*-type conduction in $CuGaO_2$ and $CuInO_2$ and to inclusively understand the defect formation behavior in $CuMO_2$ together with $CuAlO_2$. In all of $CuMO_2$, the STHs are not stabilized, and O vacancies are difficult to form. Cu vacancies in $CuAlO_2$ and $CuGaO_2$ and Ca-on-In dopants in $CuInO_2$ are moderately shallow acceptors with low formation energies, which is a reason for *p*-type conduction observed in experiments. The VBMs of $CuMO_2$ are mainly formed by Cu 3*d*-orbitals, and this result reaffirms the importance of the design concept based on orbital hybridization.

I discussed the energetics of point defects in the non-Cu-based oxychalcogenide $La_2CdO_2Se_2$ to evaluate its *p*-type dopability in terms of carrier generation and compensation. The VBM consists mainly of Se 4*p*-orbitals, the STHs are not stabilized, and the O vacancy formation energy is relatively high. Sr-on-La dopants are shallow acceptors with a relatively low formation energy. However, $La_2CdO_2Se_2$ has a relatively large vacant site, which allows Cd to enter there easily. As a result, hole compensation by Cd interstitials is problematic, making *p*-type doping of $La_2CdO_2Se_2$ difficult.

I explored new wide-gap non-Cu-based oxychalcogenides in collaboration with experimentalists. For newly discovered quaternary oxysulfide and oxyselenide, *p*-type dopability was predicted from the defect calculations. Their VBMs are mainly formed by S 3*p*- and Se 4*p*-orbitals, respectively, and the STHs are not stabilized in either system. O vacancies are relatively difficult to form in the oxyselenide but cause hole compensation in the oxysulfide. Some dopants in the oxyselenide are shallow acceptors with relatively low formation energies. These results unveil the potential of the newly identified oxyselenide as a wide-gap *p*-type semiconductor.

From the above, the following conclusions can be drawn: (i) the STHs tend to be unstable in systems where the VBM is formed mainly from orbitals other than O 2*p*, (ii) the orbital hybridization does not always suppress the formation of O vacancies, and hole compensation by other donor-type defects can also be a problem, and (iii) the design concept utilizing orbital hybridization is also effective in terms of shallow acceptor-level formation.

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).