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論 文 要 約

THESIS OUTLINE

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Thesis Outline

In Chapter 1, I explained that the recent direction of pioneering wide-gap *p*-type semiconductors has shifted from pure oxides in which O 2*p*-orbitals form the valence band maximum (VBM) to oxides containing cations with s^2 or d^{10} electronic configurations and oxychalcogenides. From the viewpoint of defect formation, the following three conditions need to satisfy to obtain 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. I sorted out that there are two types of electronic states of acceptors: weakly bound states and strongly bound states, and the latter can be further classified into acceptor-bound small polarons and acceptor on-site bindings.

In Chapter 2, the exhaustive calculations of STHs and O vacancies were performed for nine 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 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.

In Chapter 3, the point defect calculations of CuMO$_2$ (M = Al, Ga, In), a well-known Cu-based *p*-type semiconductor, provided insight into the origin of *p*-type conduction and a comprehensive understanding of the defect formation behavior in CuMO$_2$. 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 explains the *p*-type conduction observed in experiments. The VBMs of CuMO$_2$ are mainly formed by Cu 3*d*-orbitals, and the series of results reaffirm the validity of the design concept based on orbital hybridization.

In Chapter 4, the energetics of point defects in the non-Cu-based oxychalcogenide $La_2CdO_2Se_2$ were discussed 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 O vacancy formation energy is relatively high. The 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.

In Chapter 5, new wide-gap non-Cu-based oxychalcogenides were explored in collaboration with experimentalists. As a result, new quaternary oxysulfide and oxyselenide were discovered, and their *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.

In Chapter 6, the results presented above were reviewed, and the following conclusions can be drawn: (i) the STHs tend to be unstable in systems where the VBM is mainly formed 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. It was pointed out that the identification of factors to suppress (ii) hole compensation by donor-type defects is necessary to establish universal design concepts for wide-gap *p*-type semiconductors and that further studies are needed for this purpose. At least, in terms of (i) and (iii), the design concept of selecting systems in which atomic orbitals other than O 2*p* mainly form the VBM is effective. For several oxychalcogenides and binary chalcogenides, the positions of the band edges and the *p*-type doping limits due to hole compensation were aligned with respect to the vacuum level. The results indicate that it is important to consider hole compensation by donor-type native defects in addition to the band edge positions to infer *p*-type dopability. Furthermore, comparing the newly discovered quaternary oxyselenide with a related binary chalcogenide shows that the former has the advantage of a broader range of dopant choices than the latter.

In Chapter 7, the results of this thesis were summarized.