論文 / 著書情報
Article / Book Information

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Title(English)	First-principles study of hydrogen impurities in metal oxides
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Category(English)	Doctoral Thesis
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 ）

Metal oxides have a lot of fascinating applications, e.g., capacitors, sensors, solar cells, fuel cells, catalysts, photocatalysts, and semiconducting devices. Hydrogen is the most ubiquitous impurity in oxides. Once hydrogen impurities are introduced into oxides, they typically form OH^- hydroxyls. They are often the sources of n-type conductivity and hole compensation since the positively charged hydrogen, namely the proton (H^+), can cause electron doping. Thus, it is important to understand and control the behavior of hydrogen impurities to improve the lifetimes and performances of oxide-based electronic devices. Especially, since the character of hydrogen can vary from donor-like to acceptor-like, the charge transition level from H^+ to H^- (CTL(+/−)) is the key quantity to understand the behaviors of hydrogen. It has been intensively investigated both theoretically and experimentally. However, the universal understanding of hydrogen impurities in a wide variety of oxides is still not established because the number of compositions and the variation of crystal structures considered previously are limited.

In this thesis, I performed high-throughput first-principles calculations to elucidate the factors determining the formation energies, local geometries, and CTLs(+/−) of hydrogen impurities in metal oxides. Machine-learning models were also constructed to discuss the important descriptors and predict the hydrogen formation energies and CTLs(+/−) from bulk properties. The primary points of this thesis are as follows:

The automation of generating interstitial hydrogen positions is necessary for high-throughput calculations. But it is not a simple problem because small hydrogen atoms or ions can take various configurations in oxides. Thus, I firstly investigated the methodology for modeling the interstitial hydrogen impurities in a given crystal structure. It was found that (i) local minima of the electrostatic potential, (ii) local maxima of the electron localization function, and (iii) local minima of the charge density are available as candidates for the initial input positions of interstitial hydrogen for first-principles calculations combined with the geometry optimization.

Next, I performed high-throughput calculations of hydrogen impurities in 937 oxides. Their crystal structure data were initially retrieved from the Materials Project database under several conditions on bulk properties: e.g., it must be non-magnetic, non-metallic, and stable against the competing phases. The formation energies of H_i^+, H_i^0, H_i^-, and H_O^+ were calculated using the generalized gradient approximation (GGA) with the supercell approach. The bandgaps underestimated by the GGA were corrected by the non-self-consistent calculation approach using a dielectric-dependent hybrid functional. I also assessed the CTLs(+/−) from the formation energies of H_i^+ and H_i^-. It was found that the differences in formation energies and CTLs(+/−) in various oxides can be explained mostly by the host electronic structures such as the O-site potential energy and the average energy of the top of the valence band and the bottom of the conduction band.

Based on the formation energy of H_i^+, a candidate for a wide-gap p-type oxide semiconductor was found. Its theoretical bandgap largely depends on the configuration of cations, which ranges from 1.7 to 3.3 eV by calculation using the HSE06 hybrid functional. The vacancies and acceptor dopants were investigated using a pseudo-disordered phase model of the candidate oxide. It was found that n-type doping is possible because cation vacancies do not limit the controllable range of the Fermi level within the bandgap, while p-type doping is not easy because the oxygen vacancy determines the lower limit of the Fermi level to be about 0.2 eV above the VBM.

I also found that hydrogen impurities exhibit shallow donor levels in about 20% of the 937 oxides, based on the hydrogen formation energies at the GGA level and the band-edge positions determined by the non-self-consistent dielectric-dependent hybrid functional calculations. Most of such oxides contain the cations on the right side of the periodic table with large atomic numbers, e.g., Cd, In, Sb, Pb, and Bi. This is mostly because atomic orbitals of such large cations mainly construct the bottom of the conduction bands with relatively low energies.

Finally, machine-learning approaches using the least-absolute-shrinkage and selection-operator (LASSO) linear regression and random forest regression techniques were applied to the high-throughput calculation results to further understand the relationships between the hydrogen formation energies or CTLs(+/−) and the bulk properties. Descriptors related to the composition, crystal structure, band structure, local potential, electron negativity, and others were used for machine learning. The formation energies of H_i^+, H_i^-, H_O^+, and CTLs(+/−) obtained by the high-throughput calculations were reproduced by the regression models with root mean squared errors (RMSE) of 0.20, 0.55, 0.34, and 0.31 eV, respectively. Most of the important descriptors were relevant to the host band structures. Exceptionally, the depth of the electrostatic potential at the interstitial region, the oxygen concentration per volume, the mean of electron negativities, and the heat of formation were found to exhibit relatively high importance depending on the regression models.

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。
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