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題目(和文)	希土類酸水素化物中のイオン／電子的キャリア輸送とエネルギーレベルアライメント
Title(English)	Ionic/Electronic Carrier Transport in Rare-Earth Oxyhydrides and Energy Level Alignment
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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

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（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

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

Hydrogen, the lightest element composed of one proton (H^+) and one electron (e^-), is the most abundant and fundamental chemical substance and exhibits unique properties with respect to the valence state, diffusivity of ionic species, and change in the valence state through the redox reaction. Recently, solid hydrides containing hydride ion (H^-) as a constituent anion have attracted much attention for attractive properties, such as the fast H^- conductivity and high catalytic activity, which are associated with the unique features of H^-, such as the charge and size flexibility, large polarizability, capability of electron-substitution, and orbital symmetry. Whereas the understanding of the behavior of H^+ and H^0 in a wide range of host materials has made progress, regarding H^- in solids, a viewpoint from electronic energy level being never focused, should provide a new guideline to design and understand hydrides with the marked physical properties. The objective of this thesis is to provide insight into the unique properties of H^- in solid hydrides based on the electronic energy level alignment. For this objective, the modulation of the electrical property of H^--conductive REH_x and $REH_{3-2y}O_y$ involved with H^- migration is investigated. The outline of this thesis is shown in the following.

Chapter 1: The characteristics of hydrogen in various forms in solids are outlined, and in particular, the unique physical properties of solid hydrides arising from the feature of H^- are summarized. Based on these backgrounds, the objective of this thesis was described.

Chapter 2: The energy level of 1s-electrons in H^- accommodated in LaH_x ($2 \le x \le 3$) and $LaH_{3-2y}O_y$ ($0 \le y \le 1$) was estimated by photoemission (ultraviolet photoelectron, inverse photoelectron, and photoelectron yield spectroscopies) measurements and density functional theory calculations. A very shallow valance band maximum (VBM) with an ionization potential of 3.8 eV is attained in LaH_3. As hydrogen content decreases and H–H distance increases, the bandwidth of the hydrogen valence band is reduced, and the top level of the band is lowered relative to $E_{vac.}$. This indicates that the primary cause of the shallow VBM is attributed to not only the moderate electronegativity of hydrogen but also the significant bonding–antibonding interaction between neighboring hydrogens with a close separation in LaH_3. Low Φs of LaH_x and $LaH_{3-2y}O_y$ are also characteristic features observed in the electronic energy level alignment. Through the measured composition, Φs are almost constant (< 2.5 eV), and E_F position was found to be determined so that charge states of hydrogen vacancy (V_H) and substituted oxygen (O_H) are balanced. The obtained energy alignment for LaH_x and $LaH_{3-2y}O_y$ reflects the electrical properties reported in earlier work.

Chapter 3: Reversible resistive switching induced by field insertion/extraction of H^- in $REH_{3-2y}O_y$ (RE = La or Y) thin films was investigated. The current–voltage measurements revealed that the resistive switching response, hysteresis, and switching voltage vary greatly with the H^-/O^{2-} ratio in the films. Using $Ti/YH_{1.3}O_{0.85}/MoO_x$ stacking structure device, a resistive random-access memory (ReRAM) operation was observed, which is the first demonstration of H^--driven ReRAM. The bipolar-type switching with a resistance switching ratio of 1 order of magnitude over 1000 cycles was confirmed. The composition gradient of H^-/O^{2-} in $YH_{3-2y}O_y$ films, in addition to the hydrogen-absorbing ability of the top electrode, is essential for effective device operation. This finding shows that hydride-conducting solid-state electrolytes are suitable for resistive switching device development.

Chapter 4: Recently, metallic hydrides, in which hydrogens are stuffed into the lattice under high pressure, have attracted attention as superconductors with extremely high critical temperatures (T_c). As presented in Chapter 2, in view of the energy level, the electronic structure close to that of metallic hydrides is found to be attained in semiconducting LaH_3 even at ambient pressure. Even though LaH_3 is an n-type semiconductor, the shallow H 1s valence band is suitable for p-type conduction. In this chapter, p-type conduction in $LaH_{3-2x}O_x$ in a hydrogen gas atmosphere was revealed. Oxygen substitution reduces V_H acting as an electron donor in LaH_3, and the fast H^- diffusion contributes to lowering Fermi level (E_F) according to the chemical potential of hydrogen in the atmosphere. Electrical measurements suggested mixed conduction of H^- and h^+. This mixed conduction is unique in that the resulting hole carrier is associated with the electronic band derived from contributions from the conducting ion. Large-amplitude hydrogen vibration and significant atomic displacement contributing to the high H^- conductivity will hinder the h^+ transport in the H 1s band. Consequently, the mobility of h^+ is lower than that expected from the large energy dispersion of the H 1s band. The extremely fast H^- conductivity in REH_x and $REH_{3-2y}O_y$ would be correlated with the transport of hydrogen in a neutral-like charge state.

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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