

論文の内容の要旨

論文題目 First-Principles Study on Photoenergy Conversion in Semiconductors using Density-functional and Many-body Perturbation Theories

(密度汎関数理論及び多体摂動理論を用いた半導体における光エネルギー変換に関する第一原理的研究)

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Development of photoenergy conversion system is required to solve the energy problem in the world. Photovoltaics and water-splitting photocatalysis, which convert photoenergy into electricity and hydrogen fuels respectively, have been widely investigated. Since the first report of photovoltaic device in 1954, photovoltaics has been actively investigated in the scientific community. Nowadays, new emerging photovoltaic devices as dye-synthesized solar cell, organic photovoltaic, quantum-dot sensitized solar cell, and perovskite solar cell have received much attentions from the viewpoint of fabrication cost, flexibility, and tunability. To find component materials for such new devices, physical properties of a large number of organic molecules, inorganic chemical compounds, inorganic nanoparticles, and organic-inorganic hybrid materials are being investigated. As well as photovoltaics, water-splitting photocatalysis has also received considerable attention because photocatalytic water splitting is truly clean manufacturing process to generate hydrogen. In the past three decades, many semiconductors have been explored for searching highly efficient water-splitting photocatalyst. Generally, metal oxides are not suitable for visible-light absorption due to the large bandgaps, thus non-oxide materials such as (oxy)nitride and oxysulfide are attracting much interest.

To find the way to design materials with desired properties for photovoltaics and photocatalysis, it is required to understand the basic processes of photoenergy conversion. Initial processes are common in both photovoltaics and photocatalysis: the first process is photoabsorption to generate electron-hole pairs, and the second process is diffusion of carriers toward a surface of the absorber. To optimize materials with respect to photoabsorption and carrier diffusion, we have to increase our knowledge on the relationship between chemical structures of materials and physical properties such as bandgap, band bending, and carrier lifetime.

These physical properties can be understood from the electronic structure of the semiconductor, thus first-principles calculation to gain the solution of the Schrödinger equation is a powerful tool to analyze the mechanism of photoenergy conversion. One of the promising first-principles methods is Kohn-Sham approach based on density functional theory (DFT). DFT is known to be successful to describe the electronic properties of atoms, molecules, and solids. Nowadays, DFT investigations for electronic properties of materials are widely employed. However, DFT is the theory for ground states thus it does not ensure to provide correct excited-state property. Indeed, it is well known that DFT calculation has an error to predict bandgaps. Many-body perturbation theory (MBPT) is one of state-of-the-art theories to reinforce DFT calculation. MBPT introduces the interactions lacked in DFT such as correct electron-electron, electron-hole, and electron-phonon interactions. Due to the development of computational resources and simulation packages, DFT combining with MBPT is becoming powerful tool for material science.

In this thesis, first-principles studies on photoenergy conversion of three semiconducting materials using DFT and MBPT are summarized. This thesis consists of five chapters. Chapter 1 is general introduction. Photoenergy conversion systems and the initial basic processes of photoenergy conversion are summarized.

In Chapter 2, the theoretical backgrounds of DFT and MBPT are described. Kohn-Sham DFT method for ground-state electronic properties, GW approximation to provide accurate bandgaps, and Bethe-Salpeter equation (BSE) for electron-hole interactions in excited states, are introduced.

In Chapter 3, electronic and optical properties of gallium zinc oxynitride (GaN:ZnO) are studied. GaN:ZnO is a well-known overall water-splitting photocatalytic material with visible-light response. The mechanism of bandgap narrowing by alloying GaN and ZnO was investigated by calculating bandgap and band edge position for many alloy structures.

At first, different level of calculations LDA, LDA+U, and GW approximation were tested with respect to the bandgaps of GaN and ZnO. As a result, it was decided to calculate two kinds of systems: 1) slab models with more than one hundred atoms for GaN-rich solid solution (ZnO concentration $x=0.0345$) by LDA+U, and 2) smaller bulk models for both GaN-rich and ZnO-rich models ($x=0.125$ and 0.875) by GW approximation and BSE.

Doping effect on the band edge positions were investigated by slab model calculations of pure GaN and several ZnO-doped models ($x=0.0345$). Comparing ZnO-doped model with pure GaN, the bandgaps are narrowed from both conduction band lowering and valence band raising. Conduction bands minimum (CBM) is lowered by mixing O 3s orbitals into original Ga 4s and N 3s components. On the valence band maximum (VBM), the original N 2p orbital is strongly coupled with shallow Zn 3d levels (p-d repulsion). The VBM is strongly localized on the Zn-N bonds thus the number and orientation of Zn-N bonds in the crystal largely govern the energy of the VBM: larger number of Zn-N bonds and shorter Zn-N bonds lead to higher VBM energy, which results in

smaller bandgaps. On the other hand, such energy shift by the different atomic configuration was not observed on the CBM positions.

It was also found that once surface becomes O-rich and bulk becomes Zn-rich simultaneously, the downward band bending occurs. This model is consistent with previous XPS analysis indicating O-rich atomic composition at GaN:ZnO surface. Such bending promotes electron ejection to the surface while holes are migrated into the bulk region. My results suggest that the extraction of holes might be more difficult than electrons on the surface of GaN:ZnO.

Next, bandgaps of both GaN-rich and ZnO-rich bulk models ($x=0.125$ and 0.875) were calculated using GW approximation. By investigating ten different atomic configurations for each GaN-rich and ZnO-rich case, the suggestion from former LDA+U calculations were confirmed: bandgaps of GaN:ZnO are affected by the number and orientation of Zn-N bonds in both GaN-rich and ZnO-rich cases. Then, absorption spectra calculated by solving BSE were compared with the experimental spectra. For GaN-rich case, the best agreement was shown in the model with 7.8125 % of Zn-N bonds while the model with 12.5 % of Zn-N bonds was the best in ZnO-rich models. This result indicates the atomic configurations experimentally obtained are different in GaN-rich and ZnO-rich cases. I suggest such difference stems from the different experimental synthesis methods. In the case of ZnO-rich solid solution, the synthesis temperature is quite lower ($< 650^{\circ}\text{C}$) than one in the GaN-rich case ($\sim 850^{\circ}\text{C}$) in order to prevent Zn evaporation. Nitrogen atoms from NH_3 gas can diffuse actively at the higher temperature for GaN-rich one, while not in the case of ZnO-rich case at the lower temperature. Higher atomic diffusion might result in reduction of thermodynamically unpreferable Zn-N bonds.

In Chapter 4, I focused on MBPT calculation of electron-phonon (e-ph) interaction, which renormalizes bandgap and introduces lifetime broadening of electronic states. Impacts of e-ph interaction on the optical absorption and carrier lifetime were investigated in two semiconductors.

At first, I tested how e-ph interaction changes the bandgap and absorption spectrum for zinc-blende GaN, which is promising semiconductor in the field of optoelectronics. By e-ph renormalization effect, the bandgap was reduced from 3.427 eV ($\text{HSE}+\text{G}_0\text{W}_0$) to 3.300 eV ($\text{HSE}+\text{G}_0\text{W}_0+\text{e-ph}$), which is closer to the experimental gap 3.295 eV at 10 K. Moreover, the absorption spectrum by BSE calculation on the electronic structure of $\text{HSE}+\text{G}_0\text{W}_0+\text{e-ph}$ was in excellent agreement with the experimental result.

Next, I have investigated e-ph coupling effect on lead iodide perovskite. Over the last five years, perovskite solar cell employing organic/inorganic metal halide perovskite as $\text{CH}_3\text{NH}_3\text{PbI}_3$ have improved the PCE rapidly, and nowadays, the PCE exceeds 20% in solid state solar cell architectures. Time-resolved transient absorption spectra analysis by Xing *et al.* reported a long hot-hole lifetime in $\text{CH}_3\text{NH}_3\text{PbI}_3$ at valence band situated below 0.9eV from the VBM. This result suggests the possibility of further improvement of the open circuit voltage of perovskite solar cell by utilizing hot

carriers. Thus I studied the electronic structures, phonons, and carrier lifetimes of two lead iodide perovskite materials $\text{CH}_3\text{NH}_3\text{PbI}_3$, CsPbI_3 , and the charged semiconductor network, PbI_3^- .

Their band structures clearly showed that the electronic DOSs at the valence bands were relatively small in $\text{CH}_3\text{NH}_3\text{PbI}_3$ and CsPbI_3 compared with that of PbI_3^- . This difference comes from the fact that the lattice constant of PbI_3^- is quite larger ($\sim 6.7 \text{ \AA}$) than ones of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and CsPbI_3 (~ 6.0 and $\sim 6.1 \text{ \AA}$) due to the absence of Coulomb interaction with A-site cation. It reduces the antibonding coupling between I $5p$ and Pb $6s$ orbitals at the VBM. Then, carrier lifetimes from e-ph interaction were calculated for CsPbI_3 and PbI_3^- . In CsPbI_3 , long lifetime region was clearly shown upper from $E - E_{\text{VBM}} \sim -0.9 \text{ eV}$. On the other hand, in PbI_3^- , no long lifetime region was observed. This is a reasonable result since the carrier lifetime is deeply related to the electronic structure: the number of carrier decay paths is reduced in small DOS region. From the comparison between CsPbI_3 and PbI_3^- , I concluded that the origin of slow hot-hole cooling is the characteristic small DOS. As mentioned above, such small-DOS region is common in this kind of perovskite materials. It makes us to predict such a long hole lifetime also exhibits in $\text{CH}_3\text{NH}_3\text{PbI}_3$, which perfectly explains the experimental result.

In Chapter 5, concluding remark and future outlook are presented.