Quantum theory of Semiconductor-Photo-Catalysis and Solar Water Splitting

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Objectives

UV light, incident on a semiconductor-water interface, has been used to split water, but it is not known exactly how this happens or how to extend the wavelength range to the visible. The semiconductor alloy GaN/ZnO has been found promising by Domen's group in Japan. The objective of this research program is to use computational theory to help unravel how the oxidation process occurs, when photo-excitations in the semiconductor arrive at the semiconductor/water interface. What surface is most effective, how do photo-holes liberate protons from water molecules on the surface, what are the reaction sites and reaction intermediates, and what constraints must the semiconductor properties satisfy? How can we design materials to improve the efficiency and increase the wavelength range of the useful light?

Technical Barriers

Technical challenges to this kind of modeling are daunting. Density-functional theory makes band gap and self-interaction errors, and available computer power forces less-than-optimal system sizes to be modeled. Experiments are only slowly yielding microscopic details to guide theory. Water is a difficult molecule to model because of quantized nuclear motions and complicated polar properties causing bonding to be a mixture of electrostatic and covalent interactions. The relevant semiconductor surface is not yet firmly identified, and the degree of alloy disorder and surface alloy enrichment are poorly known, so that theory must attempt to answer a very large list of questions.

Abstract

Domen's group [1] found that GaN/ZnO alloys were particularly effective at absorbing sunlight and harvesting photo-holes, which then oxidize water to protons and O_2. A separate catalyst is needed to harvest the photo-electrons, which reduce the protons to H_2. The SWaSSiT* group (at Stony Brook University and Brookhaven National Lab) uses computational theory (mainly density-functional theory, DFT) to try to understand the process and how to optimize it. Most of our work, so far, has used the pure GaN (10-10) (non-polar) surface-to-water interface as a simplified model. We find this surface a particularly effective water oxidizer, since water has a strong tendency (according to theory) to dissociate into H^+ (attached to surface N atoms) and OH^- (attached to surface Ga atoms). The dissociated structure is found both for a monolayer of water at T = 0 (by static DFT), and for a thick water layer at room temperature (by DFT-driven Born-Oppenheimer molecular dynamics, AIMD). To analyze the photo-electro-chemical reaction, we make a cluster calculation, using B3LYP (partial exact exchange), explicit waters of hydration, and implicit waters represented by a polarizable medium. We propose a reaction path where the surface-bound OH^- interacts with photo-holes and water molecules. We find a sequence of four proton-coupled electron transfers (PCET). In each step, a photo-hole transfers to the surface-bound anion, releases a proton, and forms a new, bound, and hydrated, anion species: (1) O^-, (2) OOH^-, (3) OO^-, finally returning to (4) OH^-, releasing O_2 in this last step. This accomplishes the overall reaction $2H_2O \rightarrow 4H^+ + O_2$. Our attention is now turning in many new directions, some of which will be discussed. For example, the semi-polar (10-11) surface has recently been identified experimentally in powders of the alloy, and may play a role. We study its surface structures using a new DFT-based implementation of a genetic algorithm. We are starting to analyze the possible roles of semiconductor polarity in photocatalysis. We have studied the alloy thermodynamics of GaN/ZnO, and the concentration dependence of the band gap, using DFT with large supercells, supplemented by a cluster expansion and Monte-Carlo simulation. The resulting model has a stable binary compound $(GaN)_{0.5}(ZnO)_{0.5}$ which disorders above 850K, and wide miscibility gaps. Above 850K there is complete solid solubility, and materials formed above this temperature are likely to remain supercooled and completely miscible at lower T. There is significant short-range order at temperatures of 1400K and below, and a correlation between lower free-energy and larger band-gap configurations.

*Other members of SWaSSiT are Marivi Fernandez-Serra, Mark Hybertsen, Li Li, James Muckerman, Artem Oganov, Xiao Shen (emeritus), Yolanda Small, and Jue Wang.

Progress Report

As outlined in the abstract, three parts of the project were completed, another part was completed by colleagues funded by a separate DOE project, and a fifth part is underway. These are (1) studies of a monolayer of water at T=0 on the GaN (10-10) surface; (2) ab initio molecular dynamics (AIMD) for the interface of bulk water at 300K with GaN (10-10); (3) quantum-chemical

modeling of photo-hole-induced reactions which produce a likely pathway for oxidation of water into H^+ and O_2; (4) thermodynamics, local order, and band gap reduction in bulk GaN/ZnO alloys; and (5) studies of the semipolar (10-11) surface of GaN and its interaction with water.

Future Directions

We should soon be able to predict surfaces of GaN (10-11) without and with a water monolayer. We will give these to our colleague Fernandez-Serra for AIMD modeling. There are many important future directions, and we will pursue a number of them simultaneously. We expect to stimulate experiments that will help us choose the most promising directions for modeling studies. (1) Obvious future directions are studies of reaction routes on the GaN (10-11) semi-polar surface, and on surfaces of alloys, both (10-10) and (10-11). (2) A project in the advanced planning stages is the interaction of water with ferroelectric thin film surfaces with controllable polarity. (3) A project that will be initiated with a new graduate student is studies of the hole mobility, hole trapping, and hole transfer dynamics in GaN with various surface terminations, and in GaN/ZnO alloys. These projects cannot be done by the PI alone. Project (1) will probably be done in close collaboration with colleagues at BNL. Project (2) involves experimental collaborators at Stony Brook and BNL, and collaboration with SWaSSiT theorists, especially Fernandez-Serra and Oganov. Project (3) will involve collaborators at both BNL and Yale.

References

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Publication list acknowledging the DOE grant or contract

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