

Investigation of Structure and Photocatalytic Activity for Water Splitting at the Aqueous – $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ Alloy Interface

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Scientific Thrust Area: Theory and Computation

This project is aligned to the CFN Interface and Catalysis theme.

Research Achievement

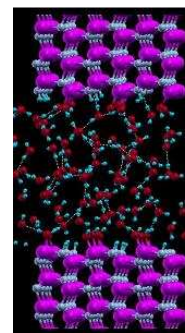
Background: Domen and coworkers have reported that a solid solution of GaN and ZnO is a stable photocatalyst, capable of splitting water under visible light [1, 2]. Of particular note is the high quantum efficiency for molecular oxygen evolution in the presence of a sacrificial electron acceptor (51% under 420-440 nm illumination) [2]. In prior work, Muckerman and coworkers explained the substantial bowing in the fundamental optical gap as a function of alloy composition using a modified Density Functional Theory (DFT) approach [3]. Meyer identified competing molecular and half dissociated phases for a water monolayer on the non-polar ZnO(10 $\bar{1}$ 0) surface [4]. In the BNL Chemistry Department, a separate experimental program (Fujita, et al) is directed to synthesis of the alloy thin films as well as structural and catalytic characterization and we maintain close connection to this work.

Scientific Questions: We focus our theoretical research on the structure of the interface and identifying the pathway for the oxygen evolution reaction. Key questions include (1) What are the plausible local composition and bonding motifs at the interface? (2) Are there localized states for the photogenerated holes that are supported by these interface structures? (3) What are the critical steps whereby electrons transfer from water fragments near the interface to fill the photogenerated holes and what is the structure of the water fragments at each step?

Research Team and Methodology: We have formed an interdisciplinary theory team spanning Chemistry and CFN from BNL and Physics at Stony Brook to tackle these questions using DFT based approaches (GGA-PBE). We model the semiconductor with thin films or small clusters and consider one or a few monolayers of water. Minimum energy structures, minimum energy pathways and molecular dynamics simulations are used to establish structures and explore dynamical processes. DFT packages used include Quantum Espresso, Gaussian and Siesta.

Water – GaN Interface: In our initial study, we have determined the structure of an adsorbed monolayer of water on the non-polar GaN(10 $\bar{1}$ 0) surface [publication below]. We find that water dissociates with a negligible energy barrier. Our analysis of the water-water interactions show that submonolayer water coverage will result in island formation due to substrate strain mediated and hydrogen bonding interactions. Because the results are very different from the ZnO case, this suggests that the surface composition of the semiconductor alloy will be a key factor determining active sites for catalytic activity.

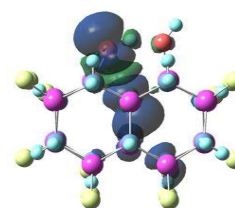
We are now probing the water interactions at the full aqueous interface. First, we have performed static calculations with three additional monolayers of water on the GaN:H₂O surface, relaxing the



MD simulation snapshot.

structures into local minima. Second MD simulations for a model system consisting of 96 H₂O molecules (equivalent to 8 monolayers of water) bounded by two GaN(10 $\bar{1}$ 0) surfaces have been done. Initial results indicate a significant change in the hydrogen bonding network in the presence of additional water. In the single monolayer case, the OH species bound to Ga atoms form hydrogen-bonded chains parallel to the surface. However both the static multilayer calculations and the first-principles MD simulations of the GaN(10 $\bar{1}$ 0) interface with bulk water indicate a stronger hydrogen-bonding interaction between bound OH species and water molecules in the overlayer or the bulk than with each other.

The initial step of the water oxidation process is being probed using a small cluster model consisting of a fragment of the GaN(10 $\bar{1}$ 0) film that has two neighboring surface Ga atom active sites. A photo-hole near the surface is simulated by removing one electron from the cluster. Two possible products of the first step of oxidation of adsorbed Ga:OH⁻ are identified: (a) a proton is transferred to the neighboring Ga:OH⁻ resulting in Ga:O⁻; (b) a Ga:OH* radical. Localization of the hole to the O p-state plays a key role.



Cluster model, OH* with hole state illustrated.

Future Work

Key issues under investigation include dynamical processes revealed by the MD simulations, the role of solvation in the oxidation process, localization of the photogenerated hole near the interface (including the possible role of defects) and development of a full oxidation pathway.

Identification of active sites at the alloy surface is crucial. We are finishing a systematic study of the ZnO/GaN alloy properties which indicates that random alloys are relatively stable against phase separation. Our study of the (10 $\bar{1}$ 0) surface shows that excess ZnO on this surface is likely. We are beginning to examine the interactions of water molecules with this surface. Alloy heterogeneity appears to make the interfacial water bonding and structure quite diverse.

With the Stony Brook part of the work developing independent funding in the past few months, a portion of the work will be performed under a newly accepted CFN User Project, “Water splitting at the surface of GaN nanoclusters and nanowires: computational modeling of the catalytic properties of GaN surfaces.”

Acknowledgements

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Publications

X. Shen, P. B. Allen, M. S. Hybertsen, and J. T. Muckerman, “Water Adsorption on the GaN (10 $\bar{1}$ 0) Nonpolar Surface,” *J. Phys. Chem. C* **113**, 3365 (2009).