# Stony Brook University
# The Graduate School

Doctoral Defense Announcement

## Abstract

Theory of ZnO and GaN: Nanostructures, Surfaces and Heterogeneous Photo-catalysis

By

**Xiao Shen**

A solid solution of wurtzite-structure GaN/ZnO absorbs light in the visible and can photo-split water. The photo-electrons reduce protons to $H_2$ when a co-catalyst is loaded. The photo-holes oxidize water into $O_2$ plus protons at the semiconductor-alloy/water interface. Microscopic details of the water oxidation process are unknown. This thesis focuses on water adsorption and oxidation on the surface of pure wurtzite GaN.

In the first part of the talk, I will present the study of water adsorption on wurtzite GaN. The structures and energetics of a water monolayer adsorbed on the $(10\underline{1}0)$ nonpolar surface of GaN are studied computationally using density functional theory (DFT). Water is predicted to adsorb dissociatively, with protons attached to the surface N atoms and hydroxide ions attached to the surface Ga atoms. The calculated energy barrier for water dissociation is negligible.

In the second part of the talk, I will present the study of a possible reaction mechanism of water oxidation at the GaN/aqueous solution interface. A cluster model consisting of a fragment of the wet GaN surface is constructed. A few explicit water molecules and a polarizable continuum model are used to simulate the aqueous environment. Based on calculations on the cluster model using hybrid DFT-Hartree Fock theory, we propose a four step mechanism for water oxidation. It starts at the hydroxide ion attached to the surface Ga atom, and contains four proton-coupled electron transfer reactions. Key intermediates, and the rate-limiting step, are identified.

**Date**: August 04, 2009
**Time**: 10:00 AM

**Program**: Physics
**Dissertation Advisor**: Philip B. Allen

**Place**: Physics B-131