HydroGEN Advanced Water Splitting Materials

Self-improving GaN/Si photocathode in PEC water splitting

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Abstract

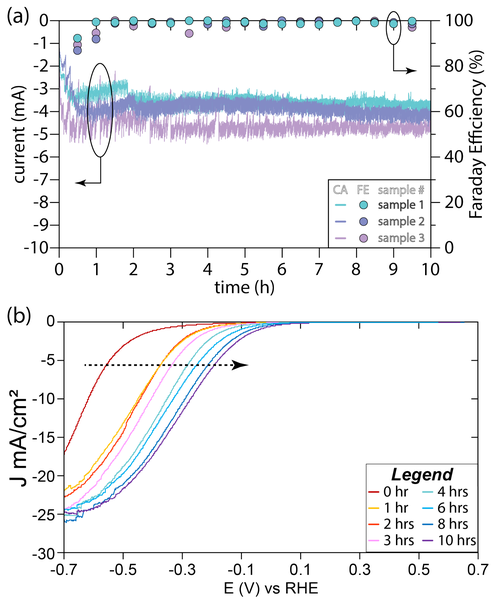
Efficiency and durability are of paramount importance to commercial use of PEC water splitting. Recent reported MBE-grown Si/GaN photocathode has demonstrated that high efficiency and durability can be attained. Our experimental study shows that as hydrogen production proceeds, as-grown GaN surface undergoes a self-improving process, and resulted in an anodic shift of onset potential, long-term stability, and improved surface catalytic property. Further analysis suggests that the observed surface change predominantly takes place at the facets containing m-plane surface, where partial nitrogen substitution by oxygen takes place at the few atomic layers of surface, leading to the improved surface stability and the catalytic performance.

Introduction

Photoelectrochemical (PEC) water splitting mimics plants to generate sustainable clean fuels using the two most abundant resources on the earth – sunlight and water. Using GaN as protective layer can effectively stabilize the Si light absorber while the near-perfect band alignment can efficiently assist the charge transfer, which results in > 3,000 hours hydrogen production under high photocurrent density and ~11.9% ABPE.

In this work, we systematically investigate the stability mechanism of GaN/Si photocathode. The results reveal a self-improving nature of GaN which is origin from the formation of gallium oxynitride during the HER.

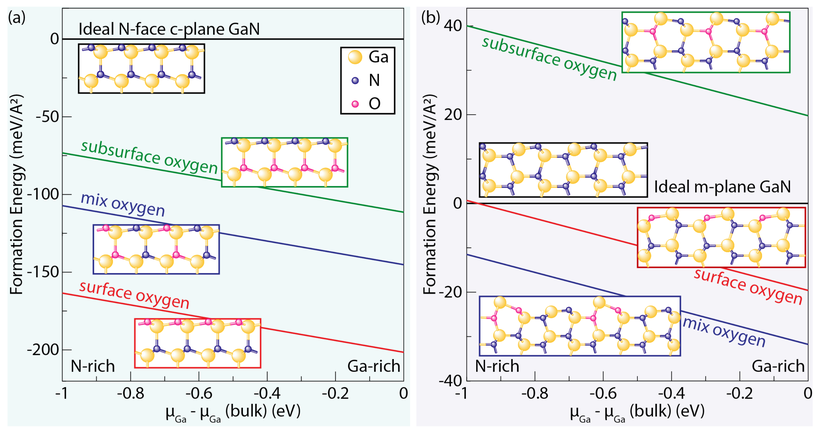
Results, Highlights, and Accomplishments



PEC performance

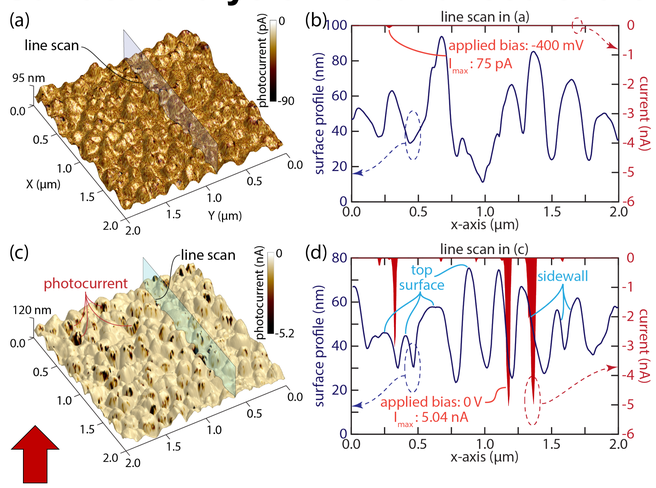
PEC results show an anodic shift of turn-on voltage over time, and saturated after first few hours. Together with the improvement of the turn-on voltage, the Faradaic efficiency also increases to 100% without applying any electrocatalysts at the surface.

DFT simulation

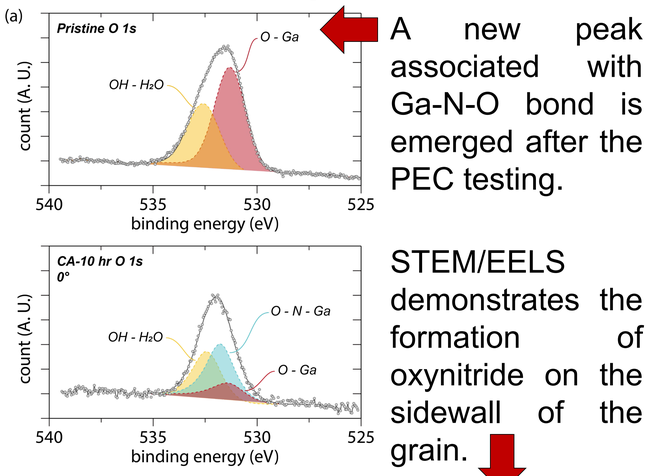


DFT calculation reveals that the formation of oxynitride on GaN exhibits an orientation dependence, and this oxynitride can further stabilize the system, and provide more active sites for hydrogen evolution reaction.

Surface analysis via advanced characterization techniques

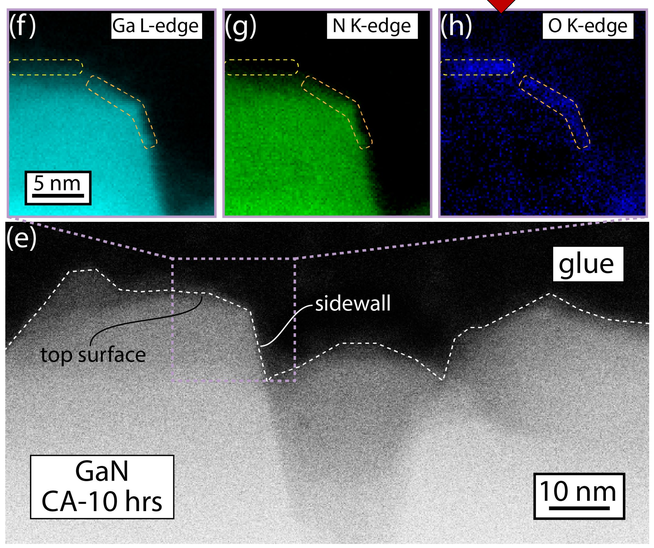


pc-AFM evidences that the surface remaining unchanged after test, but a more than two orders of magnitude increasing of the photocurrent is observed. Furthermore, most of the current comes from the sidewall of the grain, indicating an orientation effect.



A new peak associated with Ga-N-O bond is emerged after the PEC testing.

STEM/EELS demonstrates the formation of oxynitride on the sidewall of the grain.



Conclusion and outlook

In this work, we systematically investigate the stability mechanism of GaN/Si photocathode. It has been experimentally and computationally demonstrated that the orientation dependent formation of gallium oxynitride leads to a self-improving behavior.

Future work will focus on the design and fabrication of InGaN / Si double junction, which can further enhance the quantum efficiency. How to stabilize the more vulnerable In component is another challenge we will work on.

Acknowledgement

HydroGEN Advanced Water Splitting Materials Consortium

Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy

Energy Materials Network U.S. Department of Energy

BERKELEY LAB · Sandia National Laboratories · Idaho National Laboratory · Lawrence Livermore National Laboratory · SRNL