論文の内容の要旨

論文の題目:
Elucidation of electronic structure at n-GaN and electrolyte interface
（n-GaNと電解液の界面における電子構造の解明）

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Solar energy is a desired energy source due to its inexhaustibly and reducibility in CO_2 emission during energy conversion. To convert solar energy into electricity, a photovoltaic cell has been commonly installed and operated. However, we are facing with the problem of unstable energy supply such as fluctuation in time and spatially. due to chaotic natural condition. To solve the problem, the solar energy should be stored and used to respond demand. Hydrogen is a desired energy storage because it can be stored for longer time than batteries. The potential in the energy storage enables us to transport the solar energy as the hydrogen to the region where amount of solar radiation is scarce. These strengths of the hydrogen as the energy storage can stabilize energy supply in time and spatially.

Water splitting photoelectrode and photocatalyst, based on the photoelectrochemical (PEC) reaction, are the desired devices for solar to hydrogen conversion. Although the narrow band gap materials are being developed for absorbing low energy photon in solar spectrum, the reported energy conversion efficiency is still far from target due to carrier recombination. To solve the problem, carrier splitting efficiency should be enhanced by optimizing the band bending in semiconductor. However, it is difficult to control the band bending at semiconductor/electrolyte due to insufficient understanding about determinants such as surface states in semiconductor, surface adsorption and redox reactions. To solve the problem, these factors should be regulated.

In this study, n-GaN(0001)/electrolyte was used as the model case of semiconductor/electrolyte interface for water splitting to clarify the determinant of the band bending due to its defined surface of +c plane, chemical stability and band edge potential that straddles the redox potentials of water oxidation and reduction reactions. To suppress the effect of redox reaction and analyze the effect of surface adsorption, the band bending under ultra high vacuum (UHV) and water vapor was compared. Then, the effect of redox reaction was evaluated at n-GaN/electrolyte interface.

Band bending at n-GaN/H_2O adsorption layer has been determined by X-ray photoelectron spectroscopy (XPS) from the valence band maximum (VBM), which has been calculated from Ga 3d peak using the energy difference between VBM and Ga 3d ($\Delta E_{\mathrm{VBM\text{-}3d}}$). However, the several reported value for $\Delta E_{\mathrm{VBM\text{-}3d}}$ caused difficulty in clarifying the determinants of the band bending. This work validates these values which have been reported previously, by analyzing the spectrum around the VBM and its distance from Ga 3d for n-GaN(0001) surface. Adopting 17.5 eV, validated value, as $\Delta E_{\mathrm{VBM\text{-}3d}}$ suggested the origin of such band bending was Fermi level pinning to the Ga dangling bonds under UHV and the sub-surface states which cannot be compensated by H_2O under water vapor.

The band alignment at the interface between n-GaN and 1M NaOH with various treatments to define surface was investigated by observing open-circuit potential (OCP) of the GaN as a function of irradiated light intensity. For the smaller light intensity than 10^{-2} mW/cm^2, OCP value was less dependent on light intensity and it was sensitive to the surface treatment of GaN by electrochemical reducing methods, the irradiation of accelerated Ar atoms, high-energy electrons and γ-ray. The difference of pinning level among various surface treatments in same electrolyte suggested that surface states created by the treatment decided the band bending. The relationship between OCP and light intensity can be obtained without modifying the surface by photocurrent and it would be a good indicator how the surface treatment of a photoelectrode affects the photocatalytic activity.

For further discussion about the effect of surface states on the band bending, the distribution of surface states was compared with Fermi level pinning. The density of surface states was lower than detection limit of 10^{12} cm^{-2} ev^{-1} at for as non-damaged surface. However, Fermi level pinning was observed by OCP measurement. The band bending at non-damaged n-GaN/1M NaOH was determined by the surface states although the density was lower than the criterion for Fermi level pinning at metal/semiconductor of 10^{12} cm^{-2} ev^{-1}.

Based on these results, the band bending should be determined by surface states. Therefore, the band bendings at interface between n-GaN and electrolytes other than 1M NaOH should be equal. The band bendings at n-GaN/1M NaOH, 0.2M Na_2SO_4, 1M HCl or 0.5M H_2SO_4 were evaluated as 1.1-1.2 eV under dark condition. Under irradiating photon flux of 10^{11}-10^{13} cm^{-2}s^{-1}, the amount of reduction in the band bending was 0.5 eV in 1M HCl and 0.2 eV in 0.5M H_2SO_4.

The difference suggested the more photogenerated carriers accumulated in the vicinity of n-GaN/1M HCl interface than 0.5M H_2SO_4. This result suggested the surface recombination was suppressed by Cl^- which worked as hall scavenger.

These results suggest that surface states decide the band bending at n-GaN/electrolyte interface under dark condition without fast redox reaction. Under illumination, the band bending can be affected by redox reaction via suppressing the surface recombination. To optimize the band bending at semiconductor/electrolyte interface, the surface states distribution should be controlled and suppressing surface recombination by the hall or electron scavenger should be considered under illumination.