Material-dependent Photoresponse of quasi-Fermi Level in Single-crystalline Photoanodes

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One of the promising technologies that can convert the fluctuant solar energy into a storabe energy carrier, hydrogen, is photoelectrochemical (PEC) water splitting. Although many novel structures and materials have been reported, the efficiency of PEC water splitting is still inferior for practical usage. The crucial conditions for the progress of PEC water splitting are to find a semiconductor photoelectrode which has an appropriate band alignment with quasi-Fermi levels under illumination straddling the redox potentials of water as well as to understand the behavior of photo-generated charge carriers in the photoelectrodes.

The photoelectrode materials are commonly selected based on the band-edge energies, assuming a flat-band condition. However, band bending generally exists at the semiconductor/electrolyte interface as shown in Fig.1(a). This phenomenon makes the quasi-Fermi levels positioned inappropriately to split water under insufficient light intensity. The band bending is reduced when a large number of photo-generated carriers accumulate in the bulk of semiconductor as illustrated in Fig.1(b). It results in the shift of quasi-Fermi level towards the flat-band condition, allowing the water splitting reactions to take place.

In this study, we aim to explore the basic processes governing the photo-generated charge carriers in the semiconductor photoelectrode from the viewpoint of semiconductor physics. The behavior of the quasi-Fermi level of electrons with respect to the irradiated light intensity was examined for different photoanodes through the photo-induced open-circuit potential (OCP), i.e. the position of quasi-Fermi level of the majority carriers in the photoelectrode relative to the reference electrode.

Here we report the influence of light intensity on the OCP of the single crystalline photoanodes: undoped TiO₂ (rutile), 0.05 wt% Nb-doped TiO₂ (rutile), and n-type GaN on Si. A He-Cd laser (325 nm) was used as a light source. The light intensity varied in terms of photon flux from 3.9×10⁹ to 5.3×10¹⁷ s⁻¹cm⁻². All measurements were performed in 1M NaOH (pH 14) with Ar gas bubbling.

The OCP results of all photoanodes show a similar tendency as shown in Fig.2. Plateau of OCP versus light intensity is observed at the photon flux less than 10¹¹ s⁻¹cm⁻². The position of plateau depends on the surface condition of the photoelectrode and the dissolved gas in the electrolyte. When the photon flux is larger than 10¹¹ s⁻¹cm⁻², the exponential relationship is clearly observed between the photon flux and OCP. The negatively increasing OCP implies the accumulation of charge carriers in the bulk of semiconductor, resulting in the reduction in band bending, in a similar manner to solid-state junctions of semiconductors. At the photon flux of 10¹⁷ s⁻¹cm⁻², the result evidences the hydrogen evolution reaction becoming possible at the counter electrode.

The ideality factors of a diode evaluated from the slope of the plots in Fig.2 are 1.06 and 1.57 for the Nb-doped and the undoped TiO₂ photoanodes, respectively. The ideality factor of GaN photoanode, prepared by the hetero-epitaxial growth on Si, is 2.30. These results indicate that doping makes depletion region thinner and suppresses the non-radiative recombination. Besides, high crystal quality can suppress the non-radiative recombination of photo-generated carriers in the semiconductor bulk, resulting in ideality factors close to unity.

![Fig.1 Band alignment of n-type semiconductor photoelectrode in an electrolyte. (a) Under dark condition, the Fermi level of the semiconductor is in thermal equilibrium with redox potential in the electrolyte. (b) Under the strong illumination, the quasi-Fermi levels of electrons and holes energetically position above the hydrogen evolution reaction and the oxygen evolution reaction, respectively.](image1)

![Fig.2 Open-circuit potential (OCP) of 0.05wt% Nb-doped TiO₂ (blue), undoped TiO₂ (orange) and n-GaN on Si (yellow) photoanodes as a function of photon flux in 1M NaOH (pH 14)](image2)