論 文 の 内 容 の 要 旨

論文題目　Development of Novel Chalcogenide-Based Photocathodes and Construction of Reaction Systems for Water Splitting
（新規カルコゲナイド系光電極の開発及び水分解反応系構築に関する研究）

氏　名　兼古　寛之

Chapter 1: General Introduction

The modern society depends heavily on fossil fuels as energy resources. However, the energy resources are finite and usage of them has caused severe environmental problems such as the global warming due to carbon dioxide emission. Introduction of a clean and renewable energy is an urgent issue in order to avoid these risks. Recently, development of systems for hydrogen production from water and sunlight has received considerable attention because it plays an important role to construct the clean and sustainable energy system based on hydrogen as the energy carrier without emitting carbon dioxide. Among various kinds of the solar-to-hydrogen conversion systems, photoelectrochemical (PEC) cells composed of a couple of semiconductor electrodes, a photocathode and photoanode, connected in series is expected to be relatively simple and efficient because it doesn't require any electric device and can combine their individual potentials to drive water splitting reaction. Cu-chalcopyrite is known as a suitable photocathode material due to the less-expensive fabrication process, easiness in band position engineering and efficient light absorption. Especially, polycrystalline $Cu(In,Ga)Se_2$ thin films have shown the highest photocurrent value among polycrystalline materials. However, the Cu-chalcopyrite-based photocathodes developed so far have exhibited insufficient onset

potentials of photocurrent and impractical durability at the working potential of PEC cells due to the shallow valence band maximum (VBM) potential and corrosion of the photocathode surface, respectively. Consequently, PEC cells composed of the photocathode and another photoanode have demonstrated very low solar-to-hydrogen conversion efficiencies (STHs) and poor stabilities. Considering the background, the object of this thesis was determined development of a novel photocathode which shows sufficient PEC property including high durability for construction of efficient and stable PEC cells, and demonstration of overall water splitting using the PEC cells.

Chapter 2: Development of ZnSe:Cu(In,Ga)Se_2 Photocathodes

Aiming to increase the onset potential of Cu(In,Ga)Se_2 photocathodes, introduction of ZnSe to form a solid solution, ZnSe:Cu(In,Ga)Se_2, was investigated. Since ZnSe shows a deeper VBM than that of Cu(In,Ga)Se_2 by approximately 0.8 eV, a considerable shift of the VBM potential was achieved. As a result, the $(ZnSe)_{0.85}(CuIn_{0.7}Ga_{0.3}Se_2)_{0.15}$ (abbreviated as $(ZnSe)_{0.85}(CIGS)_{0.15}$ herein) photocathode exhibited a more positive onset potential than that of the $CuIn_{0.7}Ga_{0.3}Se_2$ photocathode by 0.17 V to achieve a notably high onset potential of 0.9 V_{RHE}, while it can utilize photons with the wavelength up to 900 nm. The high onset potential is suitable for the usage in PEC cells, and therefore the $(ZnSe)_{0.85}(CuIn_{0.7}Ga_{0.3}Se_2)_{0.15}$ has been found as a promising photocathode material.

A PEC cell composed of the $(ZnSe)_{0.85}(CIGS)_{0.15}$ photocathode and a $BiVO_4$ photoanode, which is known as a promising photoanode thanks to the relatively negative onset potential and high quantum efficiency, exhibited an STH of 0.91% without application of external bias voltage. The STH was the highest among the reported values at that time. On the other hand, continuous degradation in the photocurrent was observed, which is focused on in chapter 5.

Chapter 3: Development of ZnSe:Cu(In,Ga)Se_2 Photocathodes

The $(ZnSe)_{0.85}(CIGS)_{0.15}$ photocathode developed in chapter 2 has exhibited a relatively low quantum efficiencies; the induced photon-to-current conversion efficiency (IPCE) was less than 50% at 400 nm, resulting in a low photocurrent value of 7 mA cm^{-2} at 0 V_{RHE}. In chapter 3, effects of multistage deposition process of $(ZnSe)_{0.85}(CIGS)_{0.15}$ were investigated so as to increase the photocurrent value by modifying the film structure. Consequently, the bilayer structure consisting of a Ga-rich layer and an In-rich layer was found to double the photocurrent value, exhibiting 12 mA cm^{-2} at 0 V_{RHE}. The IPCEs exceeded 60% at a wide range of wavelength. A PEC cell using the bilayer $(ZnSe)_{0.85}(CIGS)_{0.15}$ photocathode showed an initial STH of 1.6%.

This chapter also demonstrated an electron-beam-induced current (EBIC) into the

photocathodes so as to reveal the origin of the high efficiency. To the best of the author's knowledge, this is the first application of EBIC measurement to a photoelectrode. Employment of Mo as a surface electrode was found to reproduce the condition of PEC reaction at 0 V_{RHE} even in the equipment for EBIC measurement kept in a high vacuum. The distribution of active region for charge separation was successfully visualized, revealing that the bilayer sample showed more uniform active area than the conventional sample. To conclude, the uniform distribution of active region contributes to the improvement in the PEC property.

Chapter 4: Development of Flexible ZnSe:Cu(In,Ga)Se_2 Photocathodes for Construction of Stirring-Free Photoelectrochemical Cells

In this chapter, effects of substrates on the PEC properties of $(ZnSe)_{0.85}(CIGS)_{0.15}$ photocathodes were investigated. Na species involved in the conventional substrate, soda-lime glass (SLG), was found to play an important role to show a high quantum efficiency and onset potential. Moreover, deposition of a thin SLG layer onto a Ti foil realized fabrication of a flexible $(ZnSe)_{0.85}(CIGS)_{0.15}$ photocathodes, which is easy to cut and bend. The easiness in cutting made it possible to construct integrated photoelectrodes composed of long and narrow strips of the photocathode and a $BiVO_4$ photoanode. The integrated photoelectrodes were found to drive overall water splitting and that the reaction rate was not affected by forced convection of the electrolyte, which can increase the net STH.

Chapter 5: Effects of RuO_2-Coating onto the Durability of the ZnSe:Cu(In,Ga)Se_2 Photocathode

This chapter focused on stabilization of $(ZnSe)_{0.85}(CIGS)_{0.15}$ photocathodes by coating the surface to suppress their corrosion during PEC reaction at a working potential of a PEC cell, around 0.6 V_{RHE}. This study employed RuO_2 as a protection layer for a photoelectrode for the first time. Because RuO_2 itself shows a relatively good activity in hydrogen evolution reaction and metallic conductivity, the RuO_2 layer can act as the surface catalyst and electron mediator as well as the protection layer. The $(ZnSe)_{0.85}(CIGS)_{0.15}$ photocathode coated with amorphous RuO_2 with a thickness of 6-10 nm exhibited almost no degradation for longer than 10 h at 0.6 V_{RHE} in the electrolytes at both pH 7 and 13. Observation of the photocathode surface revealed that no corrosion occurred at the RuO_2-coated photocathode during the PEC reaction under the harsh condition. The RuO_2 layer also showed a phenomenon of gradual increase in its catalytic activity during the reaction, called as activation. Angle-resolved X-ray photoelectron spectroscopy measurements suggested that hydroxylation of the RuO_2 surface is attributed to the activation phenomena.

The PEC cell consisting of the RuO_2-coated $(ZnSe)_{0.85}(CIGS)_{0.15}$ photocathode demonstrated a greatly improved stability and the initial STH exceeding 1%. However, there was still a meaningful

degradation in the STH observed. Analyses on the photocathode surface revealed that catalyst poisoning on the photocathode surface was caused by Bi species, which was dissolved from the $BiVO_4$ photoanode. The poisoning problem was addressed in chapter 6.

Chapter 6: Control of Cation Impurities in the Electrolyte for Long-Term Operation of Photoelectrochemical Cells

So as to suppress the poisoning phenomenon which was revealed in the previous chapter, effects of introduction of chelating resin beads into the electrolyte and surface modification of the $BiVO_4$ photoanodes with anion-conductive ionomer layers onto the stability of the PEC cells were investigated in this chapter. The chelating resin beads were expected to adsorb Bi species dissolved into the electrolyte before they were deposited on the photocathode surface. The PEC cell employing the electrolyte dispersed with the resin beads exhibited no degradation in the photocurrent for two days after the photocurrent reached plateau. It was found that the deposition rate of Bi species was greatly slowed down by introduction of the resin beads. The period of two days is the longest among other reports on PEC cells.

On the other hand, it was also been found that the relatively low concentration of Bi^{3+} species in the electrolyte facilitates decomposition of $BiVO_4$ based on a shift in the solution equilibria. Herein, the surface of $BiVO_4$ photoanodes were covered with anion conductive layers in order to block the migration of metal cations into the electrolyte. The blocked cations are accumulated in the interface between $BiVO_4$ and the ionomer layer to suppress further decomposition. Owing to the effect, the ionomer-coated $BiVO_4$ photoanodes exhibited a sufficient stability even in the resin-introduced electrolyte. Consequently, the PEC cell consisting of the ionomer-coated photoanode exhibited an improved stability in the electrolyte dispersed with the chelating resin beads.

Chapter 7: Summary and Outlooks

The current study developed a novel photocathode material, $(ZnSe)_{0.85}(CIGS)_{0.15}$, demonstrated a high durability using a surface modifier of RuO_2 and constructed PEC cells using the photocathodes and $BiVO_4$ photoanodes. The RuO_2-coated $(ZnSe)_{0.85}(CIGS)_{0.15}$ photocathode exhibited a high durability at a working potential of a PEC cell, a relatively high onset potential and a sufficient absorption edge wavelength in near-infrared region. Since it is expected that the knowledge of band edge engineering, surface protection technique and surface poisoning phenomenon is generally applicable to other photoelectrode materials, the author is confident that the thesis gives important information of further development of practical photoelectrodes and PEC cells for sunlight-driven hydrogen production to show a high efficiency and durability.