

博士論文（要約）

Development of CdTe Thin Film Photoelectrodes for Solar-driven Water Splitting

（太陽光駆動水分解に向けたテルル化カドミウム光電極の開発）

蘇 進

（Su Jin）

Department of Chemical System Engineering,
School of Engineering, The University of Tokyo

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Abstract

Increasing global energy demands and relevant environmental issues have led to a pressing need for renewable fuels that can be generated from solar energy, so as to store and use solar energy readily available upon request. Recently, there has been significant attention in photoelectrochemical (PEC) water splitting using semiconductor photoelectrodes, since this represents promising means of directly converting solar energy into chemical energy through producing hydrogen. Hydrogen produced through the water splitting using solar energy is regarded as a clean fuel because it can be made in an environmentally friendly manner and produces only water during combustion. The photoelectrode is the central part of a PEC water splitting system. For efficient water splitting utilizing sunlight, the photoelectrode must have a long absorption edge wavelength and must be able to utilize photo-excited carriers for the water splitting reactions efficiently. Chalcogenide semiconductor material of CdTe has a number of attractive properties directly applicable to PEC water splitting, such as a proper band gap of 1.5 eV and a high light absorption coefficient of $>10^4 \text{ cm}^{-1}$ below 800 nm.

Assuming an incident photon-to-current efficiency (IPCE) of unity up to the absorption edge wavelength, the photocurrent generated by CdTe photocathode could potentially be as high as 29 mA cm^{-2} under AM 1.5G light. Polycrystalline CdTe thin film with columnar structure is preferable in photoelectrodes for efficient charge separation and transfer. However, the observed photocurrent was much smaller than

this value. There is a large room to improve the PEC properties of CdTe photocathodes. Because most of photoanode are with short absorption edge wavelength, it's necessary to develop a new photoanode with a long absorption edge wavelength available in PEC cell for efficient absorption and utilization of the sunlight. For utilization of narrow band gap semiconductor materials and obtaining high solar-to-hydrogen energy conversion efficiency, the bi-photoelectrode PEC cell based on two-steps excitation composed of series-connected photocathode and photoanode is also need to be investigated. Based on the photocurrents of the photocathode and the photoanode at the same working potential, the water reduction and oxidation can separately occur on the surfaces of these couple of photoelectrodes, respectively. The operation photocurrent and working potential of the bi-photoelectrode PEC cell can be estimated from the crossing point in overlapped current-potential curves of the respective photoelectrodes, and the solar-to-hydrogen energy conversion efficiency is increased with the working photocurrent restricted by the current-matching.

In this study, a close spaced sublimation (CSS) system is constructed for CdTe thin film deposition. The PEC properties of CdTe photocathode prepared by CSS on fluorine-doped tin oxide-coated glass plate (FTO) substrate and the effects of surface modifications on the photocathodes with CdS and Pt were investigated. For further enhancement of hydrogen evolution on the CdTe photocathode, investigation about back contact for facilitated charge transfer and post-deposition annealing for more preferable structural properties of CdTe film were also conducted. The Cu/Au layer deposited between CdTe and FTO enhanced the charge transfer at the back contact

through decreasing series-resistance and Schottky barrier. The post-deposition annealing treatment with existence of a sintering additive, CdCl_2 , of the CdTe layers further enhanced the hydrogen evolution from water on the surface modified CdTe photocathode through changing the structural feature more preferable. The novel CdTe based photoanode with internal p-n junction was also investigated. The surface modification with protection layer and catalyst for water oxidation was studied. PEC cell composed of CdTe-based photocathode and photoanode for overall water splitting was examined under AM 1.5G light irradiation.

In chapter 2, photoelectrochemical hydrogen production from water using CdTe photocathodes prepared by CSS was investigated. A CdTe thin film deposited on a FTO acted as the photocathode. Surface modification of this photocathode with Pt resulted in an increase in the cathodic photocurrent from only 0.01 to 0.14 mA cm^{-2} at $0.1 \text{ V}_{\text{RHE}}$. Further surface modification with an $\sim 80 \text{ nm}$ -thick CdS layer significantly increased both the cathodic photocurrent and the onset potential from 0.14 to 6.0 mA cm^{-2} at $0.1 \text{ V}_{\text{RHE}}$ and from 0.2 to $0.6 \text{ V}_{\text{RHE}}$, respectively, under simulated sunlight. The CdTe photocathode showed virtually 100% Faradaic efficiency and a half-cell solar to hydrogen conversion efficiency (HC-STH) of 0.9% at approximately $0.2 \text{ V}_{\text{RHE}}$.

In chapter 3, post-deposition treatment and introduction of additional back contact layers on the CdTe-based photocathode were studied. The improved CdTe-based photocathodes showed a large cathodic photocurrent of 22 mA cm^{-2} at 0 V_{RHE} under simulated sunlight, and an extremely high IPCE of $>95\%$ at $560\text{--}660 \text{ nm}$ with an applied potential of 0 V_{RHE} . Structural characterization revealed that the grain structure of

CdTe thin films deposited on Cu and/or Au-coated FTO substrates was significantly influenced. These structural differences were attributed to Cu diffusion during the CdTe deposition process and to the characteristics of the interfaces between the CdTe layer and the substrate. Further investigations also determined that the CdCl₂ treatment eliminated impurities in the CdTe films. PEC measurements revealed that Pt- and CdS-modified CdTe photocathodes deposited on Cu and Au-coated FTO substrates exhibited three times higher HC-STH values than a photocathode prepared on an FTO substrate. This enhancement resulted from the improved structural properties and the facilitated charge transfer between the CdTe and the substrate through the thinning of the Schottky barrier and the relatively large work function of Au. CdCl₂ treatment further improved the extent of hydrogen evolution from water for CdTe photocathode. In addition, the HC-STH for this device were 3.7% at 0.3 V_{RHE}. The photocathodes generated relatively stable photocurrents over 70 min and hydrogen evolution with a Faradaic efficiency of approximately 100%.

In chapter 4, CdTe based novel photoanode was investigated. The photoanode was constructed thorough the chemical bath deposition (CBD) of CdS on FTO substrate followed by CSS depositon of CdTe. The CdTe layer and CdS layer form p-n junction. This CdTe/CdS/FTO electrode worked as photoanode with a long absorption edge wavelength of 830 nm available in PEC cell for efficient absorption and utilization of the sunlight. Using radio frequency (RF) magnetron sputtering deposited Ti protection layer and MoO_x thin buffer layer on the surface of CdTe/CdS/FTO electrode, the CdTe photoanode exhibited a photocurrent of 0.85 and 3.8 mA cm⁻² at 0.6 V_{RHE} and 1.2 V_{RHE}

under AM 1.5G illumination after the surface modification with $\text{Co}(\text{OH})_x$. The p-type CdTe thin film electrode can work as photoanode because of the p-n junction formed at CdTe/CdS interface which separates photo-excited carriers and forces the photo-generated holes to move towards the surface of CdTe photoanode as well as driving oxidation reaction on the electrode surface. The MoO_x buffer layer can decrease the barrier height and provide Ohmic contact at the protective layer/CdTe interface and, thus, plays a crucial role in facilitating photo-generated holes transfer to the electrode surface for improving PEC performances of CdTe photoanodes. The maximum of half-cell solar to hydrogen conversion efficiency of CdTe photoanode was 0.85% at 0.8 V_{RHE} and the Faradaic efficiency of the PEC water oxidation reaction was approximately 100%. The PEC cell composed of CdTe photocathode and CdTe photoanode resulted in overall water splitting and generated a 0.17 mAcm^{-2} , which value corresponds to solar-to-hydrogen energy conversion efficiency of 0.2%, of photocurrent without an external voltage under AM 1.5G light irradiation. This study indicates that the highly efficient charge separation at inner p-n junction structure, use of protective layer, surface modification with co-catalysts, and introduction of a high work function buffer layer are beneficial for development of photoanode for PEC water oxidation. This concept, use of p-type semiconducting materials as light absorber, can be useful for development of photoanode with wider range light absorption for more efficient solar hydrogen production. The CdCl_2 treatment could facilitate both photocurrent and onset potential of CdTe based photoanode through the increase of crystallite size of CdTe. The use of Ni and TiO_2 as an oxygen evolution reaction (OER) catalyst and protective layer

increased photocurrent; 3.8 to 5.1 mA cm⁻² at 1.2 V_{RHE} and 0.85 to 1.6 mA cm⁻² at 0.6 V_{RHE}, respectively. The onset potential of CdTe photoanode was also shifted to more preferable potential, from 0.4 to 0.2 V_{RHE}. However, the utilization of TiO₂ as the surface protection layer could not improve the durability. The initial photocurrent of the bi-photoelectrode PEC cell was 0.40 mA cm⁻² at the beginning of light irradiation, it indicated the initial STH is 0.49%. The further challenges are improvement of stability and photocurrent through surface modification with functional materials.