博士論文（要約）

Study on (Ag,Cu)$GaSe_2$ Thin Film Photocathodes for Water Splitting

（水分解のための(Ag,Cu)$GaSe_2$薄膜光カソードに関する研究）

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Abstract

Sustainable energy supply is one of the greatest challenges facing the world today. Solar-driven water splitting for hydrogen production is one of the most promising solutions for sustainable energy supply in the near future. This thesis studies the photoelectrochemical (PEC) water splitting for hygrogen evolution by sunlight using (Ag, Cu)$GaSe_2$ (ACGSe) photocathodes modified with Pt, CdS and $CuGa_3Se_5$.

As one category of efficient sunlight-absorbing materials for thin film solar cells, $CuGaSe_2$ (CGSe) is an promising candidate as photocathode for hydrogen evolution due to its high photo-absorption coefficients (ca. $10^5\ cm^{-1}$), suitable band gap (ca. 1.65 eV), usability in polycrystalline state, and high stability for hydrogen evolution in electrolyte. However, the main challenges for high-efficiency PEC water splitting on CGSe photocathode is that the valence band maximum (VBM) potential of CGSe is too low in comparison to oxygen evolution potential, and the crystallinity of CGSe is very poor due to the high melting temperature of CGSe (ca. 1050 ^oC). To improve the PEC performance of CGSe photocathode for hydrogen evolution, these two disadvantages need to be solved. Furthermore, our understanding on this material especially its PEC properties in water splitting is extremely limited in comparison to the widely studied metal oxide semiconductor electrodes. Therefore, it is important to study the effects of modification on the structural, electronic and PEC properties of CGSe electrode.

The objectives of this thesis is to improve the PEC performance of CGSe electrodes for water splitting through elemental substitution and surface modification, and study the relationship between PEC properties and film quality. The following ways have been tried in this thesis to improve the PEC properties of CGSe electrode: (1) Partial substitution of Cu in CGSe into Ag to form ACGSe thin films. (2) CdS surface modification to form CdS/ACGSe p-n heterojunction. (3) Applying two-step deposition methods to improve the ACGSe film/Mo substrate interfaces. (4) Introducing $CuGa_3Se_5$ thin layer onto ACGSe to form bilayer-textured $CuGa_3Se_5$/ACGSe thin films to modify

the CdS/ACGSe interfaces.

In Chapter 1, the necessity of sustainable energy, the properties of sunlight and potential of solar energy were introduced. The advantages of PEC water splitting, fundamentals of semiconductor and semiconductor-electrolyte interfaces were presented. Furthermore, the available material candidates for photoelectrodes and the general strategies for high-efficiency PEC water splitting were briefly reviewed. Finally, the structural and electronic properties, the advantages and disadvantages of CGSe-based semiconductor material were introduced in details.

In Chapter 2, the main preparation methods used in this thesis were introduced. The radio frequency magnetron sputtering and vacuum co-evaporation methods using a molecular beam epitaxy (MBE) system, which were used to preparing the Mo substrates and ACGSe thin films for this thesis, were introduced in details. In addition, the selection of hydrogen evolution catalyst and the PEC deposition method were briefly introduced.

In Chapter 3, the effects of Ag partial substitution on the structural, electronic and PEC properties of CGSe were studied. The structural and electronic results showed that Ag partial substitution largely increased the grain size and positively shifted the valence band maximum (VBM) potential of CGSe. The PEC results on bare ACGSe and Pt modified ACGSe showed that ACGSe with Ag/Cu+Ag ratio ca. 5% showed the best PEC activity. The prepared Pt/ACGSe (Ag 5.9%) showed a photocurrent of ca. 3.8 mA cm^{-2} at 0 V_{RHE} and onset potential of 0.51 V_{RHE} (defined at cathodic photocurrent of 0.05 mA cm^{-2}), which shows an obvious improvement compared with the Pt/CGSe (ca. 2.0 mA cm^{-2} at 0 V_{RHE} and onset potential of 0.42 V_{RHE}). The possible mechanisms for the improved PEC performance on the ACGSe electrode were discussed.

In Chapter 4, surface modification of ACGSe electrode with CdS was applied to further improve photocurrent of ACGSe. A Pt and CdS modified ACGSe (Ag 5.9%) electrode (Pt/CdS/ACGSe) showed a cathodic photocurrent of 6.2 mA cm^{-2} at 0 V_{RHE} and an onset potential of 0.67 V_{RHE} under simulated sunlight illumination in 0.1 M Na_2SO_4 (pH 9.5), which showed obvious improvement than that of Pt/ACGSe (Ag 5.9%) without CdS modification. The calculated band alignments at

solid-liquid interfaces showed that CdS modified sample showed an increased thickness of depletion layer, which in principal could faciliate the charge separation.

In Chapter 5, the Pt/CdS/ACGSe electrode was further improved by applying two-step co-evaporation method. A Pt and CdS modified two-step deposited ACGSe showed a cathodic photocurrent of 8.1 mA cm^{-2} at 0 V_{RHE} and an onset potential of 0.70 V_{RHE} under simulated sunlight illumination, and reached a maximum solar energy conversion efficiency in applied bias photon-to-current efficiency (ABPE) of ca. 1.2% at 0.3 V_{RHE}. Further, a Pt/CdS/ACGSe deposited by two-step method showed a stable cathodic photocurrent contributing to hydrogen evolution for over 4 days without clear decrease.

In Chapter 6, the Pt and CdS modified, two-step deposited ACGSe was further modified by introducing a $CuGa_3Se_5$ thin layer onto ACGSe to form $CuGa_3Se_5$/ACGSe bilayer thin film electrodes. With Pt, CdS and $CuGa_3Se_5$ modification, the Pt/CdS/$CuGa_3Se_5$/ACGSe bilayer electrode with $CuGa_3Se_5$ deposited for 15 min showed a photocurrent of 8.3 mA cm^{-2} at 0 V_{RHE} and an onset potential of ca. 1.0 V_{RHE}, which reached a maximum ABPE of ca. 1.8% at ca. 0.35 V_{RHE}. Moreover, a Pt/CdS/$CuGa_3Se_5$/ACGSe electrode showed a cathodic photocurrent contributing stoichiometric hydrogen evolution from water for ca. 20 days without clear decrease, indicating that ACGSe electrode with suitable modification can act as a highly stable photocathode for PEC hydrogen evolution.

In Chapter 7, the main conclusions for this thesis and several promising aspects for future studies were summarized. In future, constructing a dual-electrode system using the modified ACGSe photocathodes in this thesis and the state-of-the-art photoanode such as Ta_3N_5 to realize bias-free overall water splitting under sunlight irradiation is certainly worth trying.

Keywords: Silver; Copper Gallium Selenide; $CuGaSe_2$; CdS; $CuGa_3Se_5$; Ordered Defect Chalcopyrite; Vacuum Co-evaporation; Photocathode; Photoelectrochemistry; Hydrogen; Water Splitting; Solar Energy Conversion.