**Research Report**

**Chalcopyrite CuGaSe2 thin film for photoelectrochemical water splitting into hydrogen**

Shigeru Ikeda1 and Shogo Ishizuka2

1Department of Chemistry, Konan University, Kobe 658-8501, Japan

2Research Institute for Energy Conservation, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8568, Japan

Copper chalcopyrite compound CuGaSe2 (CGS) is a promising material for its application to photoelectrochemical (PEC) water splitting into H2. In this article, we firstly review operating principle and measurement methods of PEC water splitting by using semiconductor-based electrodes. Then, studies on PEC H2 evolution over the CGS-based photocathodes were reviewed. For realizing efficient PEC H2 evolution, surface modifications with a CdS layer and nanoparticulate Pt catalytis were indispensable. Moreover, insertion of a Cu-deficient layer and its further modification with Rb are found to be effective for improvements of PEC properties. Since present photoelectrodes have poor resistances under an operating bias, further functionalization is required to improve the long-term durability for practical uses.

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**1. Introduction**

According to recent statistics [1], the current (2021) global primary energy consumption is 595 EJ (exajoules) per year. Despite the slowdown in economic activity caused by the COVID-19 pandemic, the figure has increased by nearly 15% over the past decade. Meanwhile, the amount of solar energy reaching the earth's surface is enormous, estimated to be about 3×106 EJ per year, and efficient use of this energy is essential to solving our energy and environmental problems. In this context, technologies that use photocatalysts made of semiconductor powders or photoelectrodes made of semiconductor thin films to photodissociate water into hydrogen, a form of chemical energy that can be stored, are attracting attention as a new way to use solar energy as a complement to photovoltaic power generation. Hydrogen is a clean energy that produces only water as a by-product. It is used as a fuel gas in fuel cells and shows promise for applications in thermal power generation and various types of engines. However, since hydrogen is currently produced from fossil resources such as natural gas and naphtha, there is strong support for the idea of producing hydrogen from water using solar energy.

The water-splitting reaction is a typical uphill reaction with a large positive Gibbs free energy of 237 kJ mol-1. In water splitting using a photocatalyst or photoelectrode, the reaction is driven by carriers (electrons and holes) generated by band-gap excitation of the semiconductor by externally supplied light. The generated carriers migrate to reaction sites on the surface within their lifetimes, reducing and oxidizing water, resulting in water splitting. The loss due to recombination of carriers at this time is large, and it is important to have a "mechanism" that promotes efficient separation of carriers and reactions on the surface in order to function as a highly active photocatalyst or photoelectrode.

In our research on photocatalysts and photoelectrodes, we have been studying photoelectrodes, in particular semiconductor photoelectrodes, that reduce water to produce hydrogen. This article focuses on CuGaSe2 (CGS), a chalcopyrite-type compound semiconductor, and introduces its functionality as a hydrogen-evolving photoelectrode, including basic information on photoelectrochemical measurements and their evaluation methods.

**2. Fundamentals of water-splitting reactions using photoelectrodes**

**2.1 Operating principle**

　When a semiconductor electrode is immersed in an electrolyte, electrons are transferred between the semiconductor and the electrolyte so that its Fermi level (*E*F) is in equilibrium with the redox potential of the electrolyte [2]. Since the concentration of electrons and holes in the semiconductor is finite and the band position (potential) at the solid-liquid interface is fixed, electron migration causes band bending similar to a Schottky junction. As a result, the electrons among the photogenerated carriers accumulate on the surface of a p-type semiconductor electrode, whereas the holes accumulate on the surface of an n-type semiconductor electrode. If the carriers accumulated on the surface have sufficient potential to reduce or oxidize water, the semiconductor electrodes become a photocathode (Fig. 1(a)), which reduces water to produce hydrogen, and a photoanode (Fig. 1(b)), which oxidizes water to produce oxygen. In this process, holes transferred to the electrode in the p-type semiconductor and electrons transferred to the electrode in the n-type semiconductor are transferred to the counter electrode via a backside electrode and external circuit, where they are used for reduction or oxidation reactions. Since the hole or electron potential on the counter electrode coincides with the Fermi level of the photoelectrode in the photoexcited state, in order for such carriers to have the potential to reduce or oxidize water, it is necessary to use semiconductors with a relatively large band-gap energy (*E*g). Most semiconductors with a band gap in the visible light region do not have the potential to allow a water-splitting reaction to proceed at a single photoelectrode. In such a case, if the photocathode and photoanode are connected in series (tandem) and carriers with sufficient potential for water-splitting reactions are generated by two stages of photoexcitation, the water splitting can proceed without external bias (Fig. 1(c)). Although the tandem configuration has the disadvantage of doubling the number of photons required to acquire one electron used in a reaction (from one photon to two photons), it has the advantage of using semiconductors that can effectively utilize visible light, which includes much of sunlight. In fact, recent calculations on the solar energy conversion efficiency of photoelectrode systems predict that the maximum conversion efficiency obtained from water splitting using a single photoelectrode is only about 13%, whereas the value exceeds 21% if two stages of photoexcitation in a tandem configuration are used [3].

**2.2 Experimental methods and efficiency**

The simplest configuration for water splitting using a photoelectrode is a two-electrode system consisting of a photoelectrode and a counter electrode, as shown in Fig. 1, or, in the case of a tandem configuration, a photocathode and a photoanode. Focusing on one electrode (referred to as the "working electrode"), in order to evaluate its intrinsic properties, it is necessary to measure the current at the exact potential (current-voltage characteristic), but this is not possible in a two-electrode system where the potential depends on the characteristics of the counter electrode. In electrochemical systems, it is necessary to accurately measure the potential relative to the electrolyte solution to investigate current-potential characteristics, and a three-electrode system with a reference electrode is used for this purpose. In a three-electrode system, the potential of the working electrode is controlled using a potentiostat relative to the reference electrode, and the potential of the counter electrode is fed back so that the current passing through the counter electrode matches the current produced on the working electrode. If an electrode that always has a fixed potential relative to the electrolyte is used as a reference electrode, the potential relative to the electrolyte can be accurately determined (an example is an electrode with an Ag/AgCl wire dipped in a saturated KCl solution (silver-silver chloride electrode), which always has a value of +0.199 V relative to a standard hydrogen electrode). The potential of the working electrode measured against a reference electrode (in this case a silver-silver chloride electrode) ($E\_{ref}$) can be converted to potential for a reversible hydrogen electrode (RHE) ($E\_{RHE}$) based on the following equation.

$$\begin{array}{c}E\_{RHE}=E\_{ref}+0.199+0.059×pH\#\left(1\right)\end{array}$$

Using $E\_{RHE}$, even when water splitting is performed with electrolytes of different pH, the equilibrium potentials for hydrogen and oxygen evolution $E\_{H^{+}/H\_{2}}$ and $E\_{O\_{2}/H\_{2}O}$ are 0 V and +1.23 V, respectively, with respect to the RHE standard, making it easy to compare the results.

The solar to hydrogen efficiency (STH) of water splitting using photoelectrodes is the energy of hydrogen produced by water splitting relative to the energy of sunlight (expressed as a percentage). Assuming the incident solar energy per unit area is 1.0 kW m-2 at air mass 1.5 global tilt (AM1.5G), the area of the photoelectrode is S m2, and the hydrogen evolution rate in water splitting is *r*H2 mol s–1, the STH is expressed as follows [4].

$$\begin{array}{c}STH \left(\%\right)=\frac{r\_{H\_{2}}×237}{1.0×S}×100\#\left(2\right)\end{array}$$

$r\_{H\_{2}}$ is the hydrogen evolution rate actually obtained in a two-electrode system, that is, the hydrogen evolution rate obtained in a system that combines all elements including the overvoltage of the electrode reaction. In this case, if half the number of electrons per second (e–/2 mol s–1) passing through the external circuit (the conductor between the two electrodes) is equal to $r\_{H\_{2}}$, i.e., if the Faraday efficiency (*η*F) is 1, the STH can be obtained from the observed current.

As described above, the current-potential characteristics measured in the three-electrode configuration do not allow the STH to be determined directly from the obtained current-potential curve, since feedback by the potentiostat is required. However, if the photoelectrode used as the working electrode generates hydrogen or oxygen under sunlight (AM1.5G) irradiation at a given potential where water splitting does not proceed in the dark, it is possible to estimate a hypothetical STH ignoring the counter electrode reaction (overvoltage) from the product of the deviation from the equilibrium potential ($E\_{H^{+}/H\_{2}}$ or $E\_{O\_{2}/H\_{2}O}$) and the photocurrent [5]. This is called “half cell (HC)-STH” because the efficiency of only one reaction is evaluated. For a photocathode with an electrode area of *S* m2, if the operating potential during hydrogen evolution is $E\_{RHE}$, the deviation from the equilibrium potential is $E\_{RHE}-E\_{H^{+}/H\_{2}}$ (=$E\_{RHE}$), and if the current at that time is *I* A, the HC-STH is defined as follows.

$$\begin{array}{c}HC-STH=\frac{E\_{RHE}×I×η\_{F}}{1.0×10^{3}×S}×100\#\left(3\right)\end{array}$$

Here again, if *η*F is 1, the HC-STH can be determined from the current measurement.

**3. Water reduction reaction using CGS polycrystalline thin films**

**3.1 Photoelectrodes from CGS thin films: surface modification**

　Attempts to use CGS as a photoelectrode for water-splitting hydrogen evolution are few compared to its application to solar cells [6] and other studies on thin films of Cu-chalcopyrite compounds, but there are some reported examples. Marsen et al. investigated the evolution of H2 in an acidic electrolyte (0.5 M H2SO4) using a CGS thin film deposited on a Mo-coated soda lime glass (Mo/SLG) substrate utilizing a multisource deposition technique, evaluated the current-potential characteristics of CGS thin films without surface modification under simulated sunlight (AM1.5G), and reported an onset voltage of 0.136 V for the photocathode current and a saturation current density of 10.6 mA cm−2 at -0.66 V [7]. Unfortunately, there was no qualitative or quantitative analysis of the gases generated, and in the region where the thin film functions significantly as a solar energy conversion device, i.e., where the HC-STH is estimated (*E*RHE > 0 V), almost no current was observed. Because the CGS surface has very low catalytic capacity for water reduction, it is doubtful that any significant photocurrent is observable unless the potential is made more negative than the hydrogen evolution equilibrium potential $E\_{H^{+}/H\_{2}}$.

Moriya et al., using the same multisource deposition technique as Marsen et al., created a photoelectrode from a thin film (Pt-CGS) supporting nanoparticulate Pt with low hydrogen evolution overvoltage on the surface of a CGS thin film deposited on a Mo/SLG substrate [8]. The results showed that a photocathode current attributed to hydrogen evolution appears starting at potentials more positive than the equilibrium potential of hydrogen evolution (~0.7 V vs RHE) (Fig. 2(a)). Furthermore, it was possible to improve the photocathode current significantly by creating a photoelectrode from a thin film (Pt-CdS/CGS) in which a 40 nm thick CdS layer is laminated on the surface of the CGS by chemical bath deposition (CBM) before supporting the nanoparticulate Pt (Fig. 2(b)). The HC-STH estimated from the current-potential polarity and *η*F (90%) was about 0.8%. CdS modification of Cu chalcogenide thin films by CBD to form good pn junctions is a well-known technique for solar cells, and on various occasions the facilitatory effect of modifying Cu chalcogenide thin film photoelectrodes with nanoparticulate Pt and a CdS layer to improve photoelectrode properties has been demonstrated in thin films such as CIGS [9], CuInS2 [10], and Cu2ZnSnS4 [11]. From these facts, we can conclude that (1) since there are deep defect levels on the CGS surface, even if a catalyst for hydrogen generation such as nanoparticulate Pt is supported, carrier recombination through these defect levels is not suppressed, and a large photocurrent cannot be obtained; but (2) the introduction of the CdS layer passivates such defects, and the resulting pn junction spatially separates the carriers, thereby suppressing carrier recombination, resulting in a significant improvement in photocathode properties.

**3.2 Effect of insertion of a Cu-deficient layer (CDL) [12]**

A study on high performance in CGS solar cells revealed that it is possible to improve the open circuit voltage (VOC) and short circuit current density (*J*SC) by actively introducing a Cu-deficient layer (CDL) composed of CuGa3Se5 at the CdS/CGS interface [13]. Aiming for a similar facilitatory effect, i.e., a shift of the photocathode current onset potential toward the positive potential side due to hydrogen evolution and an enhancement of the saturation current, we used the multisource deposition technique to prepare polycrystalline CGS thin films (CDL/CGS) coated with CDL at different thicknesses and performed surface modification with Pt-CdS to investigate the effects of the CDL layer on photocathode current onset potential, HC-STH, and other properties.

The CDL/CGS thin films were fabricated on Mo/SLG substrates using a multisource deposition technique with three different deposition source types and deposition temperatures. We prepared a CGS thin film without surface CDL (type-A) and three CGS thin films covered with CDL at different thicknesses (type-B: < 50 nm, type-C: 50 nm, type-D: 200 nm), deposited a 60 nm CdS layer on each thin film by the CBD method, loaded the nanoparticulate Pt, and evaluated the current-potential characteristics under simulated solar irradiation (AM1.5G). For the type-C and type-D thin films, photoelectrodes with a thicker (90 nm) CdS layer were also prepared and compared. We were able to obtain significant photocathode currents from all the photoelectrodes, and we confirmed that the value of *η*F was approximately 1 based on the time change in the amount of evolved hydrogen measured at a constant potential (0 V vs RHE) and half the number of electrons passing through the external circuit. The HC-STH estimated from the obtained current-potential curve (calculated assuming that *η*F = 1) is shown in Fig. 3(a), and the onset potential of the photocurrent is shown in Fig. 3(b). Compared to the results for type-A without CDL, type-B, type-C, and type-D with CDL clearly demonstrated a significant improvement in both characteristics. The effect of the thickness of the CdS layer on type-C and type-D was also significant, with further improvements to both characteristics when a thicker rather than thinner CdS layer was used. The maximum value of HC-STH (6.6%) was obtained by type-C, and the most positive photocathode current onset potential (0.93 V vs RHE) was obtained by type-D.

Fig. 3(c) shows the relative positions of the band-edge energies of CdS, CDL, and CGS [13]. Although CDL is thought to include heterogeneous phases, the figure assumes CuGa3Se5. The insertion of the n-type CuGa3Se5 causes the pn junction to shift from the CdS-CGS interface to the CDL-CGS interface. As a result, the CDL blocks the diffusion of holes generated by the CGS to the CdS side, and the CDL increases the spatial distance of the electrons injected into the CdS side. These effects are thought to suppress carrier recombination at the CdS-CGS junction interface and improve the properties described above. The reason why the HC-STH of type-D is lower than that of type-C may be due to the absorption of incident light by the thicker CDL layer. Based on these observations, we prepared a photoelectrode with a CDL thickness similar to that of type-C (tens of nm) and a thicker CdS thickness (120 nm). After loading the nanoparticulate Pt, we evaluated the photocathode properties and found that a HC-STH exceeding 7% was achieved.

**3.3 Effects of Rb doping [14]**

　We investigated the effect of adding Rb to CDL/CGS thin films by integrating RbF into the CDL/CGS thin film deposition process. We evaluated the photoelectrode properties of Rb-doped CDL/CGS thin films modified with Pt-CdS (120 nm thick) and found that HC-STH was improved under conditions where more Rb was doped in the CDL, reaching a maximum value of about 8%. The details are under investigation, but so far we have observed the following: (1) the addition of Rb has no effect on the diffusion of SLG-derived Na; (2) Rb diffuses relatively well into the CDL, but hardly diffuses into the CGS layer; and (3) in terms of photoelectrode characteristics, a relatively high HC-STH is obtained with a thinner CDL than the Rb-free CDL/CGS.

**4. Durability of the photoelectrode**

When used as a photocathode for a water splitting system in a tandem configuration, depending on the photoanode used on the other side (oxygen evolution side), the semiconductor photoelectrode should be able to handle about half of the voltage (1.23 V) required for the water-splitting reaction. In a three-electrode system, this is equivalent to requiring efficient hydrogen evolution at an operating potential of about 0.6 V vs. RHE. Our CGS-based photoelectrode described in the previous section is quite capable of hydrogen evolution at such potentials, judging by its current-potential curve, but at the same time a marked decrease in hydrogen evolution is observed [12]. Similar deterioration in photoelectrode characteristics has also been observed in PT-CdS-modified CuInS2 [15,16] and Cu2ZnSnS4 thin films [17]. In the case of the Pt-CdS/Cu2ZnSnS4 thin film, comparing the shape of the electrode surface before and after the reaction, the CDs layer, which uniformly covered the surface of the Cu2ZnSnS4 before the reaction, changed to a shape in which discontinuous particles were deposited, and comparing the XP spectra of the 3d orbital of Cd before and after the reaction, a CdO peak appeared after the reaction that was not observed before the reaction, suggesting that the degradation of the CdS layer was a factor in the degradation of the photocathode properties (Fig. 4) [17]. As a way to curb this degradation, attempts to coat the CdS surface with another compound layer as a “protective layer” have been made on a photoelectrode system based on Cu2ZnSnS4. So far significant effects have been observed when coating with a In2S3 layer [17] as well as HfO2 [18,19]. Since the introduction of the protective layer does not (presumably) select the target photoelectrode, it would seem to be a method that could also be applied to the CGS system described here.

　A simple idea to improve stability is to avoid using unstable CdS. We have reported that In2S3 laminated by the CBD method can be used as an alternative layer for CdS in CuInS2 photoelectrode systems [16,20]. And with regard to CGS, recent studies in solar cells have reported that ZnSnO is an n-type layer that provides better cell characteristics than CdS [21]. Such alternative oxide-based materials are expected to be suitable for use in photoelectrode systems in terms of stability.

**5. Conclusion**

In this article we introduced water-splitting hydrogen evolution using semiconductor photoelectrodes, focusing on a system based on the chalcopyrite compound CuGaSe2, including its operating principle and methods of measurement and evaluation. In terms of actual usage, the hypothetical efficiency HC-STH in the system introduced in this paper is in the single digit range, and it is clear that a major breakthrough is needed to improve it. In addition to the stability (deterioration) issues introduced here, it has not been shown how to use rare elements (for example, Pt catalysts) or design tandem configurations on a large scale easily (at low cost), so there are many challenges to be overcome. Some would say that a large number of challenges is a blessing for researchers. We hope that this article will inspire some readers to enter this field as new researchers and help move us further along the path to practical application.

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