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Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Conformal chalcopyrite based photocathode for solar refinery applications

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ARTICLE INFO

Article history:

Received 6 September 2015

Received in revised form

17 January 2016

Accepted 27 January 2016

Available online 10 February 2016

Keywords:

PEC cells

CIGSe

Protecting overlayers

Water splitting

Solar hydrogen production

Stainless steel

ABSTRACT

Photoelectrochemical properties of conformal photocathodes based on chalcopyrite built-in on flexible stainless steel foils are shown to give current density level higher than 30 mA cm^{-2} (0 V_{RHE}). These conformal photocathodes can become elements for developing new concepts for PEC cells to obtain solar fuels. The influence on the PEC characteristics of the protective anticorrosion layer based on TiO_2 film deposited by atomic layer deposition technique at very low temperature, $200 \text{ }^\circ\text{C}$, and using TiCl_4 precursor are analyzed and discussed particularly taking into account the charge transport mechanisms through this layer. Likewise, buffer layer between the used n-type layer and the protective one such as i-ZnO and AZO layers have also been considered to facilitate high efficient photocathode design adaptable for new solar refinery applications for water splitting or CO_2 photoreduction. Improved photocurrent values are obtained with TiO_2 protective values of 100 nm.

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1. Introduction

The identification of stable and inexpensive p-type photocathode materials constitutes a key issue for developing photoelectrochemical (PEC) cells available for implementing new concepts of solar refinery producing hydrogen from water splitting as well as other fuels or chemicals from carbon dioxide reduction. Aside reliable and enduring materials and/or photocathode structures, the development of reliable PEC cells and modules is open to new concepts beyond the usual planar structures commonly reported up to now in the literature. Furthermore, aside these aspects, for commercially viable PEC devices, the overall solar-to-chemical conversion efficiencies are not the only essential parameter. Indeed, other crucial features such as the stability of the device, the use of inexpensive available materials or the manufacturing process employing easily scalable, reproducible, and economical techniques become essential too.

In this panorama, despite silicon band gap, 1.1 eV, does not fit adequately with the theoretical band gap for having maximum absorption from the solar spectra [1], P-type silicon has been extensively investigated as a candidate material [2,3]. Likewise, tunable band gap systems, like III–V semiconductors such as GaInP_2 or, alternatively some metal oxides such as Cu_2O can also be optimized to act as reliable photocathode [4,5]. Nevertheless, any of these proposed materials gather all the requirements for fulfilling conditions -efficiency, low cost, flexible layers,...- for developing adequate conformal enduring electrode structures.

Unlike the previous shown materials, chalcopyrite-type thin film materials, exemplified by CuInS_2 , $\text{CuIn}_x\text{Ga}_{1-x}\text{S}_2$ (CIGS) or $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGSe), are Cu-based materials that offer band gap energies around 1.5 eV and thus higher potential solar conversion efficiency. CIGSe has recently shown promising activity as a PEC photocathode [6] as well as the kesterites CZTS [7] which is composed of only inexpensive and readily available elements, since indium and gallium are replaced by zinc and tin which makes it very attractive in view of large scale applications for replacing CIGS or CIGSe. This alternative is structurally similar to CIGS or CIGSe and has also a direct band gap of ca. 1.5 eV although, nowadays, its solar efficiency is still limited below 16% [8,9]. As thin film layers, they can be growth on different substrates such as glass, FTO or flexible metallic foils to define conformal cathode structures. In fact, these photocathodes based on p-type

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chalcopyrite layers prepared by inexpensive and scalable techniques need also the presence of n-type buffer layers to promote charge separation through the resulting p–n heterojunction. Typically very narrow CdS layers and the less commonly used ZnS or In_2S_3 are used as n-type overlayers. These layers can, in turn, be completed with some protective and conductive layers usually based on zinc oxide with different doping level, aluminum is often used, for facilitating the electron extraction and hence improving the PEC photocurrent for inducing reduction at the cathode surface. However, these layers are not protective enough against corrosion in acid media. Consequently, in all cases, these chalcopyrite based cathode structures require a complementary anticorrosive overlayer that must also be compatible with the flexibility imposed by the metallic foil substrate.

Herein, we report a study on chalcopyrite based photocathodes prepared by inexpensive and scalable techniques on flexible substrate for having conformal cathode structures for future PEC cell design in solar refinery applications. We investigate the role of the different layers used to complete the heterojunction and we further demonstrate the ability to improve and stabilize the photocurrent delivered by chalcopyrite electrodes by protecting their surface using atomic layer TiO_2 deposition overlayers at low temperature for preventing any temperature effect on the previous deposited layers and maintaining the mechanical robustness required for the use of flexible metallic foil.

According to the efforts performed in the photovoltaic field to fabricate chalcopyrite absorbers different technological approaches can be used being electrodeposition and sputtering procedures ones of the best performing considering cost and efficiency. Likewise, different chalcopyrite compositions can be used modifying their semiconductor properties. Among them, CIGS, CIGSe and CZTS kesterites based on abundant elements are the most highlighted. Due to their high absorption coefficients, tunable band gap values (1.0–2.4 eV) by changing In/Ga and/or Se/S ratios, and suitable band alignment for water reduction, these materials are also attractive to be used as photocathodes for H_2 production from water.

In this contribution, focused in optimizing the functionality of TiO_2 layer deposited by atomic layer deposition (ALD) as protective layer for chalcopyrite, we have centered our efforts on CIGSe layer deposited by sputtering as p-type absorbing layer. As ohmic electrical contact we have used molybdenum according the standard route used for the photovoltaic thin film industry. So, for having a flexible structure, these layers were implemented on a molybdenum coated stainless steel foil cover with a chromium buffer layer [10].

To complete the photocathode structure, a PN junction is formed depositing a thin n-type CdS layer following the same criteria than those justifying to design the chalcogenide based photovoltaic device, facilitating the electron hole pair separation induced by the electric field of the space charge zone. This approach involves an appreciable improvement of photocurrent as well as onset potential compared to those of unmodified films.

However, unlike the photovoltaic device, the photoelectrochemical functionality requires to be coated by an anticorrosion protective layer that, at the same time, guarantees the highest values of minority carrier transference from the absorber chalcopyrite layer to the electrolyte.

In this context, TiO_2 is recognized as an adequate material as protective layer due to their characteristics in acid and basic electrolyte and also presents an adequate alignment of its conduction band with the CIGSe/CdS structure [7,11]. Nevertheless, it is well known that at room temperature, considering the wide band gap of the TiO_2 (> 3 eV), the charge transport mechanisms of this material corresponds rather to a nearly insulator dielectric in which the electrical conductivity is very low, that can induce

electrical performance losses modifying the expected photoelectrochemical properties. It should be observed that the conduction current of these layers, at normal applied electric field, could be very small because conductivities could inherently be low depending on the defect densities (i.e. oxygen vacancies). Assuming TiO_2 film thicknesses between 10 and 100 nm, electrical fields around 10^5 – 10^6 V/cm can be estimated through the film, being enough to have noticeable conduction current through the film. So, the conduction mechanisms through these layers could be electrode-limited or bulk-limited. The former mechanism depends on the electrical properties at the electrode-dielectric interface whereas the bulk-limited conduction mechanism depends on the electrical properties of the dielectric itself. Bulk-limited conduction is directly related to the trap level, trap spacing, trap density, carrier drift mobility, dielectric relaxation time, and the density of states in the conduction band. These parameters concern to the film thicknesses as well as to the deposition conditions.

On the other hand, substrate flexibility and mechanical robustness, number of layers and thickness could also be a parameter to take into account.

Therefore, several relevant questions concerning TiO_2 thickness itself, or the need to maintain the ZnO buffer layer and AZO top contact to increase charge transfer efficiency arise in order to define the best flexible Cu-chalcopyrite based photocathode configuration.

2. Experimental

Photoelectrodes were fabricated onto flexible stainless steel (SS). Consequently, samples with/without i-ZnO and AZO (Al:ZnO) layers, and with TiO_2 layer thicknesses of 10 nm, 50 nm and 100 nm were prepared in order to evaluate the effect of these layers on the final PEC performances. Thicknesses and characteristics of the CdS and ZnO layers have been chosen from the background of photovoltaic routes.

- Chalcopyrite layer deposition on flexible substrate: CIGSe absorbers were prepared onto 0.3 mm thick stainless steel foil substrates (coated with Cr and Mo) via sequential DC magnetron sputtering deposition (AC450 Alliance Concepts) using Cu, Cu–Ga (50–50%) and In targets (99.99% purity all of them). Reactive annealing under Se atmospheres of the sputtered metallic stacks was used to produce the absorbers. The final compositions were: $\text{Cu}/(\text{In} + \text{Ga}) = 0.90$ and $\text{In}/(\text{In} + \text{Ga}) = 0.28$, and was kept constant in this study. After the thermal annealing, the CIGS absorbers were etched by the classical KCN route (aqueous solution 10% m/v, 25 °C, 120 s), in order to remove possible unwanted Cu_xSe secondary phases at the surface [12].
- CdS deposition: CdS was deposited 60 nm thick by Chemical Bath Deposition (CBD) from CdSO_4 and thiourea precursors aqueous solutions, at 75 °C and pH=11, using the methodology reported elsewhere [13].
- AZO and ZnO deposition: immediately after CdS growth, the solar cells were completed by DC-pulsed sputtering deposition of i-ZnO (60 nm) and AZO (Al:ZnO, 300 nm) as transparent conductive window layer (Alliance CT100).
- Protective TiO_2 overlayer deposition by ALD: samples were simultaneously introduced in a R200 Picosun Atomic Layer Deposition system at 200 °C using TiCl_4 and H_2O precursors at 19 °C in successive pulses in a 8 mbar N_2 flow atmosphere, reaching a growth rate of 0.27 Å/cycle. Some samples were grown simultaneously on silicon substrates to complete characterization of TiO_2 overlayer. Layer thickness was measured by evaluating the reflected spectra with a Sensofar

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