Solar water splitting with earth-abundant materials using amorphous silicon photocathodes and Al/Ni contacts as hydrogen evolution catalyst

F. Urbain [a,*], V. Smirnov [a], J.-P. Becker [a], U. Rau [a], J. Ziegler [b], F. Yang [b], B. Kaiser [b], W. Jaegermann [b], S. Hoch [c], M. Blug [c], F. Finger [a]

[a] IEK-5 Photovoltaik, Forschungszentrum Jülich, D-52425 Jülich, Germany
[b] Institute of Materials Science, TU Darmstadt, D-64287 Darmstadt, Germany
[c] Evonik Industries AG, CREAVIS – Science to Business, D-45722 Marl, Germany

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ABSTRACT

An all earth-abundant and precious metal-free photocathode based on a low-temperature fabricated amorphous silicon tandem junction is demonstrated to be an efficient device for solar water splitting. With a particular designed Al/Ni layer stack as photocathode/electrolyte contact an onset potential for cathodic photocurrent of 1.7 V vs. RHE and a saturation photocurrent density of 7.2 mA/cm^2 were achieved. For a high-cost alternative with a Ag/Pt layer stack an even higher photocathode performance is demonstrated. Above all we present an approach for a dedicated photovoltaic and electrochemical development for solar water splitting.

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1. Introduction

The increasing energy demand is one of our society's major future challenges [1]. The need to draw on cost-effective, environmentally benign and efficient energy concepts is more omnipresent than ever before [2,3]. Solar-driven water splitting, a process that mimics natural photosynthesis, provides a viable example of an ecofriendly energy concept as it converts solar energy into a storable and clean chemical fuel, namely hydrogen. To be competitive with fossil fuels or hydrogen production by other means, this process must however become highly efficient and low-cost. Semiconductor based photoelectrochemical systems emerged as adequate candidates and have been attracting considerable interest among research groups worldwide [4,5]. Both photocathodes and photoanodes are under examination in the literature [6]. Examples for investigated photoelectrodes are III–V semiconductors (e.g. InP [7], GaP [8,9], GaInP$_2$ [10]), crystalline Si [11–13], group VI-dichalcogenides [14–17], CdS coated CuGaSe$_2$ [18], and nanostructured WO$_3$/BiVO$_4$ [19]. Practical water splitting however remains challenging due to the stringent requirements that photoelectrodes have to fulfil:

- Generation of a photovoltage well above 1.23 V, which is the minimum thermodynamic potential difference under standard conditions to produce H$_2$ and O$_2$ from water (disregarding overpotential losses in the range of >0.6 V) [20].
- Generation of high photocurrents, which is necessary because the efficiency of the water splitting process is determined by the photocurrent density provided by the photoelectrode at the respective required photovoltage [21].
- Chemical stability under the rough conditions present during gas evolution in aqueous electrolytes. Alternatively, the photoelectrode has to be covered by a protective coating [22].
- Low cost fabrication of the photoelectrodes because the technical and commercial viability is closely linked to the cost-effectiveness of such systems.

Considering this broad range of demands, thin film silicon presents an adequate semiconductor material and has recently acquired a leading position in water splitting applications [23–25]. It offers several advantages over the aforementioned semiconductors, as it is a low-cost material, which can be fabricated in multijunctions to provide high open-circuit voltages (above 1.8 V) [26] in combination with high short-circuit current densities (above 8 mA/cm^2), along with fill factors exceeding 70% [27].

Inspired by its beneficial properties, we report herein on the development of efficient and precious-metal-free amorphous
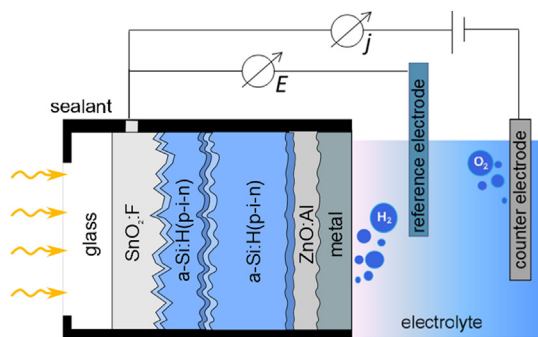
Figure 1. Schematic drawing of the photoelectrochemcial measurement set-up consisting of: the a-Si:H/a-Si:H photocathode (working electrode), the reference electrode (Ag/AgCl/3 M KCl), the electrolyte (0.1 M KOH), and the counter electrode (coiled platinum wire). The potential is denoted by E and j is the photocurrent density.

silicon tandem junction based photocathodes (a-Si:H/a-Si:H) specifically adapted for solar water splitting. As contrasted with related pioneering studies where mainly off-the-shelf devices have been used [28–30], and where the adjustment of the photovoltaic parameters of the photoelectrode was not in the focus of research, our development intended to specifically tune both, the electrochemical and the photovoltaic parameters of the photoelectrodes for water splitting. The integrated photovoltaic-assisted electrolysis device, examined in this study and schematically depicted in Figure 1, offers the advantage that the photovoltage and the photocurrent generated by the solar cell are available for the electrolysis independent of the energy band positions at the solid/liquid interface. In contrast to the photovoltaic-assisted photocatalysis [19], the solar cell and the catalysts could therefore be developed individually. Thus, the photovoltaic and the electrochemical parts of the device, such as the catalysts for the H_2 (HER) and the O_2 evolution reaction (OER), respectively, can be adapted and combined in a flexible way. An additional advantage of the device configuration shown in Figure 1 is that the incident light directly enters the solar cell and is not attenuated by the surrounding electrolyte medium, by a co-catalyst or by evolving gas bubbles. Notwithstanding this, the issue of chemical stability has to be taken into account, as the solar cells needs to be protected from the direct contact with the electrolyte. This was realized using protective metal layers.

The photocathode optimization comprised three development steps: the pure photovoltaic optimization step, which included the development of two different types of tandem solar cells: tandem cells with high photocurrent densities of 8.4 mA/cm^2 (and 1.8 V) and tandem cells providing high photovoltages over 1.9 V (and 7.7 mA/cm^2). Our approach involved improvement in the properties of individual functional layers of a solar cell: thickness variation of the p-type doped layers, integration of n-type hydrogenated microcrystalline silicon oxide (μc-SiO$_x$:H) alloys as intermediate reflecting layers between a-Si:H sub-cells and variation of the deposition process parameters of the intrinsic absorber layers. In the second step, both tandem solar cell types were compared in terms of their performance as photocathodes in a photoelectrochemical measurement set-up. In the third step, we intended to improve the metal contact at the photocathode–electrolyte interface. Layers of Ag, Al, Ni, and Pt were evaluated with respect to photocurrents and onset-potentials for cathodic currents. We found that a stack of metals is necessary to simultaneously combine good light-reflection back into the photocathode, low overpotential losses for the hydrogen evolution reaction (HER), and good chemical stability.

2. Experimental

2.1. Preparation and characterization of a-Si:H/a-Si:H tandem solar cells

All a-Si:H layers were deposited by a plasma enhanced chemical vapor deposition (PECVD) technique in a multi chamber system. For the intrinsic a-Si:H absorber layers a mixture of silane (SiH$_4$) and hydrogen (H$_2$) gases was used. For the p- and n-type layers, trimethylborane (TMB), carbon dioxide (CO$_2$), methane (CH$_4$) and phosphine (PH$_3$) gases were added to the silane-hydrogen mixture. An excitation frequency of 13.56 MHz was applied for all depositions. The a-Si:H material optimization was mainly performed as a function of the substrate temperature T_s and silane concentration SC, defined as the ratio between the SiH$_4$ flow and the total gas flow. Series of two types of tandem junction solar cells were made: (i) for the high voltage cells top and bottom a-Si:H cells were deposited at T_s of 130 °C at a SC of 4%. (ii) For the high photocurrent cells, top and bottom a-Si:H cells were deposited at 130 °C with SC of 4% and 180 °C with SC of 10%, respectively. The cells were deposited in a p-i-n-p-i-n superstrate configuration, as schematically shown in Figure 1, with an electron beam evaporated metal reflecting layer as back contact, defining the area (1 cm^2) of the individual cells. A 80 nm thin sputtered aluminium doped zinc oxide/silver (ZnO:Al) layer is deposited between the silicon and the metal layer to reduce optical losses in the device [31]. In the tandem device, the bottom cell thickness was 400 nm and the top cell thickness was 110 nm. The p- and n-doped layers are deposited at a substrate temperature of 180 °C. Since T_s is varied for the deposition of the intrinsic a-Si:H layer, a waiting time of 30 min between the layer deposition was implemented in order to maintain the required temperature of the substrate. All solar cells denoted as "cell A, B, D, E, F" were deposited on 100 cm^2 fluorine-doped tin oxide (SnO$_2$:F) coated glass substrates with a native texture (Asahi VU) and "cell C" was deposited on a 100 cm^2 texture-etched aluminium-doped ZnO:Al coated glass substrate.

Photothermal deflection spectroscopy (PDS) was performed to measure the absorption spectra of the intrinsic a-Si:H layers, which were deposited on glass substrates. From these spectra the gap energy E_{04} with a PDS absorption coefficient of 10^4 cm^{-1} was extracted, which serves as a measure for the optical band gap of the intrinsic a-Si:H layer. Solar cells were characterized by current–voltage (J–V) measurements under AM 1.5 illumination (100 mW/cm^2) using a double source (Class A) sun simulator, and by quantum efficiency (QE) measurements.

2.2. Photoelectrochemical measurements of photocathodes

The photoelectrochemical performance of the photocathodes was evaluated at room temperature in an aqueous 0.1 M KOH solution using a three-electrode configuration [32], by means of cyclic voltammetry and potentiostatic measurements. The photocathode was illuminated by a sun simulator (Newport Oriel LCS-100) with AM 1.5 G filter (100 mW/cm^2). The potential of the working electrode was controlled by a potentiostat (Gamry Reference 600). The set-up of the home-made electrochemical cell consisted of a Teflon cell body and three electrodes: the working electrode (a-Si:H/a-Si:H photocathode, 8 mm inner diameter O-ring sealant), a platinum wire as counter electrode, and a Ag/AgCl/3 M KCl reference electrode (CH-Instruments). The electrical contact to the SnO$_2$:F coated substrate was made by a silver paste. Figure 1 schematically shows the tandem junction solar cell configuration used in the photoelectrochemical arrangement. Different metal contact layers at the rear side of the photocathode (in contact with the electrolyte) were deposited by electron beam evaporation. The respective overpotentials of single metal layers deposited on