Abstract — One of the main problems of renewable energies is storage of the energy carrier. For long-term storage, solar fuels seem to be a good option. Direct solar water splitting could play an important role in the production of these solar fuels. One of the main challenges of this process is the charge separation and collection at the interfaces. The knowledge on photovoltaic (PV) junctions can be used to tackle this challenge. In this work, the use of doped layers to enhance the electric field in an a-SiC:H photocathode, and the use of thin-film silicon multijunction devices to achieve a stand-alone solar water splitting device are discussed. Using a p-i-n structure as a-SiC:H photocathode, a current density of 10 mA/cm$^2$ is achievable. The p-i-n structure proposed also indicates the suitability of traditional PV structures for solar water splitting. In addition, hybrid devices, including a silicon heterojunction PV device, are proposed. A combination of the a-SiC:H photocathode with a nc-Si:H/c-Si is demonstrated and potential STH efficiencies of 7.9% have been achieved. Furthermore, a purely PV approach such as a triple junction a-Si:H/nc-Si:H/c-Si:H solar cell is demonstrated, with solar-to-hydrogen (STH) efficiencies of 9.8%.

I. INTRODUCTION

Easily accessible and reliable sources of energy are one of the main needs of our current societies. Until recently, fossil fuels have been the option of choice when trying to cover our energy needs. However, fossil fuel resources are depleting. Instead, renewable energies offer a cleaner and more sustainable way to cover our energy needs. One of the main problems of renewable energies is the intermittent nature of its sources, creating the need for storage. In particular, solar energy has two kinds of variations that may occur: daily variations caused by clouds and day-to-night changes; and seasonal variations concerning the changes in irradiation between summer and winter. While batteries can cover the first kind of variation, the second needs a cheaper and more energy dense way to store energy [1].

An alternative option is to use so-called solar fuels. This process consists on producing hydrogen using sunlight, which can be directly stored or further combined with CO$_2$ to produce other hydrocarbons. Direct hydrogen production using solar water splitting methods has attracted considerable attention in the last years due to its potential to provide a simple and elegant solution for hydrogen production using solar energy [2]. Photoelectrochemical (PEC) methods of solar water splitting are one of the most studied fields of direct solar water splitting since the first experiments performed by Fujishima and Honda [3].

PEC production of hydrogen is based on a semiconductor, which absorbs light producing an electron-hole pair. These charge carriers are separated inside the semiconductor and reach the interfaces, where they are able to drive the water splitting reaction. There are several conditions for a semiconductor to be suitable to be used for PEC devices: good optical properties, good charge separation, correct band alignment with respect to the potentials of water splitting, and chemical stability. In addition, materials need to be earth-abundant for it to be economically feasible. Therefore, this field has mainly focused in finding the best material for solar water splitting [2,4,5].

In addition, the water splitting reaction needs an electrochemical potential to be applied, which equals the thermodynamic 1.23V of the water splitting reaction plus the overpotential associated with losses in different parts of the system. Therefore, the practical voltage needed for the water splitting reaction to happen is 1.6–2V, depending on the catalyst and electrolyte used. This needed voltage motivated the possibility to use multijunction devices to achieve the desired voltage. These can either consist of 2 photoelectrodes [6], a photoelectrode connected with a solar cell, or a solar cell by itself [7].

In this work, several approaches both from the PEC and PV perspective are presented and compared. Examples of how to improve a PEC device based on amorphous silicon carbide (a-SiC:H) by enhancing the electric field are presented. a-SiC:H was chosen as the material of this study due to its relatively low bandgap and good chemical stability [8,9]. In addition, the application of multijunction PV devices for direct solar water splitting will be discussed.

By combining the PEC expertise on the water splitting reaction with the knowledge of the PV field on semiconductor physics and device design, direct solar water
splitting can achieve good solar-to-hydrogen (STH) efficiencies. In addition, by using earth-abundant materials, these devices can also be economically feasible. In conclusion, this approach is able provide a potential solution to the seasonal storage problem, making solar energy more attractive for grid integration.

II. MATERIALS AND METHODS

Plasma Enhanced Chemical Vapor Deposition (PECVD). The a-SiC:H, a-Si:H, nc-Si:H and nc-SiO_{2}:H presented in this work were deposited using Radio Frequency Plasma Enhanced Chemical Vapor Deposition (RF-PECVD). Asahi UV-type, consisting of a textured glass with an FTO coating, was used as a substrate for the photocathodes, while float zone wafers were used for the multijunction cells based on crystalline silicon. They consisted of either p-type 100 oriented or n-type 111 oriented wafers. The precursor gases used were SiH_{4}, CH_{4}, H_{2} and CO_{2}. Boron doping for the p-type layers was done including B_{2}H_{6} gas, and phosphorous doping for the n-type layer was done by including PH_{3} gas. Different layers (p, i, n) were deposited in different chambers of an Electtrorava cluster PECVD tool to avoid cross contamination. The front contact of 300nm Al was deposited using electron beam evaporation in a Provac evaporator, and then a silver wire was attached to it using carbon paste. As a back contact and back reflector, a combination of 300nm Ag, 30nm Cr and 500nm Al was used.

TiO_{2} deposition and catalyst. A titanium oxide (TiO_{2}) layer of 35nm was deposited using an in-house Atomic Layer Deposition (ALD) system. During deposition, the substrate temperature was 200°C. Tetrakis (dimethylamino)-titanium (TDMAT) and water were used as a precursors for the Ti and O, respectively. The growth rate was 0.6-0.8 Å per cycle. The samples were further annealed at 300°C for an hour. Pt catalyst was deposited using a PREVAC sputtering tool, with sputtering with radio frequency (RF) power of 100W from a Pt pure target for 18s. The thicknesses of Pt was 1nm.

Solar cell characterization. EQE was measured with an in-house system in the PVMD group, TU Delft. It consists of a Xe lamp attached to a monochromator to change the light wavelength, and measure the output current and voltage. A calibration diode was used for correction of the spectrum. The solid state measurements of the JV characteristics were done under a double lamp Class AAA Wacom solar simulator. The temperature of 25°C, at Standard Test conditions (STC), was maintained by a cooling system integrated in the measurement stage. The short circuit current was normalized using the EQE output.

PEC measurements. The JV characteristic in a PEC setting was measured using an aqueous 2M potassium hydrogen phthalate (Alfa Aesar, 99.99%) solution at pH 4 as electrolyte. A 3 electrode measurement with an Ag/AgCl reference electrode (XR300, Radiometer Analytical) and a Pt wire counter electrode were used. The solar simulator was a Newport Sol3A Class AAA with lamp power provided of 450W. The illumination area in contact with the solution was a 3mm radius circle, with a total area of 0.283cm². Voltage and current were measured and controlled by an AG&G potentiostat. The basic schematic of how this photocathode would look like during a 3-electrode measurement is depicted in Figure 1. 2-electrode measurements were also performed using an IrO_{2} counter electrode, to be able to predict the performance of the integrated device.

Figure 1. Schematic representation of the 3-electrode photocathode configuration

III. RESULTS AND DISCUSSION

A. The PEC approach: a-SiC:H photocathode

Traditionally, research in the field of PEC has been focused on the choice of a semiconductor that is able to absorb enough light to produce charge carriers to drive the reaction, on the band alignment of this semiconductor with respect to the water splitting potentials, and on the production of enough voltage to cover the 1.23V necessary to drive the reaction plus the overpotential caused by extra losses [2,11].

However, recently the attention started to shift into looking at the device configuration, including methods to extract the charge carriers from the materials more efficiently, like using smart doping strategies. Abdi et al. [10] included a gradient tungsten doping it a BiVO_{4} photoanode. Han et al. [8] introduced a gradient doped p-SiC:H layer in an a-SiC:H photocathode. The inclusion of doped layers and junctions allow a better charge separation, enhancing the open circuit voltage and photocurrent created in the system.
The electric field inside the a-SiC:H photocathode can be improved by the introduction of an n-type nc-SiO₂ layer. Since in that case a p-i-n junction is formed, a so-called buried junction is formed. In this junction, the band alignment of the photocathode material becomes secondary. A conceptual representation of the bandgap diagram of a device with and without an n-layer is shown in Figure 2.

![Figure 2. Comparison of the energy band diagrams of an a-SiC:H photocathode and a n-type gradient doped layer.](image)

The effect of including a n-SiO₂ layer has been tested by comparing the performance of a bare p-i photocathode (A) with the one including the n-layer in contact with the electrolyte (B). In addition, the same comparison on performances has been done including a gradient p-doped layer in between the p and i layers, with (D) and without (C) the n-layer, as illustrated in Figure 3.

Figure 3 shows in addition the JV characteristic of these junctions measured as a PEC device. Both the inclusion of an n-layer and a p-gradient doped layer shifted the offset potential, considered as the potential at which the photocathode starts to produce current, by approximately 0.5V. However, the inclusion of both the gradient doped region and the n-layer does not further improve the PEC performance. These results suggest that the inclusion of either a p-type gradient doped layer or an n-layer improves the separation of charge carriers and collection in the interfaces, and reduces recombination on them. The highest saturation current is obtained when the gradient p-doped layer is not included. This gradient region is deposited a higher compared to the intrinsic layer. As a result, more defects in the form like void or boron atoms are incorporated. This will enhance recombination in this region and, therefore, will deteriorate the photocurrent performance. In addition, this gradient p-layer introduces an additional parasitic absorption of the incident light. Finally, the interface between the photocathode and the electrolyte seems to be improved by the inclusion of the n-layer, resulting in higher currents. Therefore, it is recommended to improve the electric field by introducing an n-layer rather than by including a gradient p-doped region in the front.

To further improve the a-SiC:H photocathode, the optimum thickness of the absorber i-layer was found to be 150 nm and the minimum necessary thickness for the n-layer was determined to be 20 nm. With these characteristics, current densities higher than 10 mA/cm² can be reached.

![Figure 3. Schematic illustration and PEC results of the p-i a-SiC:H photocathode (A) p-i-n photocathode (B), p-grad. p-i photocathode (C) and p-grad. p-i-n photocathode (D).](image)

However, the a-SiC:H does not have the necessary potential produced to split the water by itself, and therefore a multi-junction approach is necessary. A solar cell is integrated at the back of the photocathode, which would absorb the transmitted spectrum and create the necessary potential to drive the reaction. This solar cell has been specially developed for this purpose, and the detailed analysis of it has been presented elsewhere [12]. Since the two elements are in series, the operational point would be the intersection between the two J-V characteristics, as shown in Figure 4. The current density can be further translated into solar-to-hydrogen (STH) efficiency by multiplying it by the thermodynamic potential of H₂ of 1.23V and dividing by intensity of the the incoming light [13]. The resulting STH efficiency of the combined system would thus be 7.9%, which is relatively high in the solar water splitting field [7].

Since the a-SiC:H photocathode has practically the same p-i-n structure of a thin-film silicon solar cell, it can also be monolithically attached to the double junction cell. This
approach simplifies the proposed device and potentially reduces the losses due to cables and other factors. This approach is explored in the following section.

Fig. 4. Schematic and JV characteristic of the nc-Si:H/c-Si heterojunction solar cell and of the p-i-n a-Si:H photocathode. The crossing point of both curves will be the operational point. Note that the a-SiC:H has been measured in a 2 electrode configuration using an IrOx counter electrode.

B. The PV approach: Thin-film silicon multijunctions

By adding an n-layer to a p-i junction, it becomes apparent that the p-i-n optimized structure is essentially the same as that of a conventional thin film silicon solar cell [14]. Therefore, the photoelectrochemical approach for water splitting shifts to the simple use of a solar cell as photoelectrode, in what can be called a direct PV/electrolysis device.

An important factor to take into account when designing the appropriate solar cell for solar water splitting is that the practical voltage of 1.6–2V is needed to drive the water splitting reaction. Therefore, the use of multijunctions becomes necessary[7]. Among the most remarkable examples of this concept are Khaslev and Turner [6] for their GaAs/GaInP2 device with over 16% STH efficiencies, and more recently, Urbain et al. [7] with a triple and quadruple junction thin film solar cell with a STH efficiency of 7.8%.

Within this concept, thin-film silicon solar cells are considered an attractive option mainly due to their flexibility of design. Several configurations can be possible to reach the necessary bandgap. The proposed configurations here are an a-Si:H/nc-Si:H/nc-Si:H triple junction cell and heterojunction solar cells such as an a-Si:H/nc-Si:H/c-Si triple junction, as illustrated in Figure 5. While a-Si:H/nc-Si:H/c-Si can have a better solar spectrum utilization, the a-Si:H/nc-Si:H/nc-Si:H is easier to realize due to the absence of heterojunction interfaces that can lead to high recombination rates.

Figure 5. Schematics of the two proposed triple junction cells for solar water splitting: a) a-Si:H/nc-Si:H/nc-Si:H thin film solar cell and b) a-Si:H/nc-Si:H/c-Si heterojunction solar cell

The JV characteristic of the a-Si:H/nc-Si:H/nc-Si:H triple junction solar cell is illustrated in Figure 6. This configuration is able to reach 1.95V of open circuit voltage and 9.28 mA/cm² of short circuit current density. When combining the PEC performance of this cell with the IrOx characteristic, the reached current is 7.5 mA/cm², which would correspond to a device STH efficiency of 9.23%.

The other option possible is to use a triple junction that stacks a micromorph solar cell on top of a silicon heterojunction (SHJ) cell. This device will thus form an heterojunction between the thin film and crystalline silicon. A similar structure was already proposed in 1988 for water splitting by Sakai et al. [15]. Initial testing of these heterojunction devices resulted in an a-Si:H/c-Si solar cell on an n-type 111 oriented wafer. Including some interface engineering between the subcells, a cell with VOC of 1.43V,
Direct solar water splitting can provide an alternative route to store solar energy by producing hydrogen that could be stored or further converted into hydrocarbons. Among the main challenges for this process are besides the choice of material, the device design to extract the charges from these devices. Charge separation and collection remains one of the main challenges in the field of direct solar water splitting, and needs to be tackled in order to find a feasible device for solar water splitting.

In this work, it is shown that the application of layer-configurations known in the PV field such as the introduction of doped layers or the use of multijunctions, can highly enhance the efficiency of the devices used for this applications. As an example, the introduction of an n-layer in an a-SiC:H photocathode is shown to improve the open-circuit voltage and saturation current that can be extracted from this material. In addition, the use of multijunction solar cells is shown to be able to provide a bias free device that can efficiently produce hydrogen.

REFERENCES


III. Conclusions

FF of 51.2% and current density of 10.3 mA/cm² was obtained. Although there is still room for improvement, and the deposition of a triple junction a-Si:H/nc-Si:H/c-Si is still an ongoing activity, these results show the potential of triple junction with for heterojunction silicon cells to obtain high voltages and reasonably high current densities. Therefore, the possibilities for efficient solar water splitting can be realized with novel triple junction structures.

![Fig. 6. JV characteristic measured as a PEC and solid state device of an a-Si:H/nc-Si:H/nc-Si:H solar cell in comparison to an IrOx counter electrode in pH 0, and the equivalent STH efficiency in which these currents translate.](image)