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The effect of the illumination intensity on the performance of Si multijunction based integrated photoelectrochemical water splitting devices

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Abstract

We present a study of the effect of illumination intensity on the performance of a photovoltaic-biased electrochemical (PV-EC) device for solar hydrogen production based on a triple junction thin film silicon solar cell. The influence of the illumination intensity was studied for the solar cell as well as for an integrated PV-EC device. We show that while the open circuit voltage decreases with a reduction in intensity, the triple junction solar cell still provides a sufficient voltage to drive spontaneous water splitting. Moreover, a slight improvement in the fill factor at lower intensities can relax the requirements to the utilized co-catalysts. As a consequence, the difference in the performance of PV-EC devices featuring very active (Pt/RuO_2) and less active (Ni/Co_3O_4) catalyst materials decreases when the illumination intensity is reduced.

Keywords: Solar Water Splitting, Solar Fuels, Silicon, Solar Cells

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1. Introduction

Over the past years, the hydrogen production by light induced water splitting has attracted significant attention [1].The electrolysis of water requires a minimum thermodynamic potential of 1.23 V. Practically, however, additional overpotential losses in the order of typically 0.5 V are present [2]. One possibility to supply the required

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energy for water splitting is the utilization of multijunction photovoltaic devices. Mainly two types of multijunction solar cells have been demonstrated to allow for spontaneous water splitting: III-V [3-6] and silicon based solar cells [7–13]. Thin film silicon technology provides the advantages of a low cost and scalable photovoltaic solution. Moreover, solar cells and modules can be combined in tandem, triple or quadruple junction architectures with an open circuit voltage (V_{OC}) in the range from 1.5 to 2.8 V [13-17]. The successful application of these cells in integrated photovoltaic-biased electrochemical (PV-EC) devices for light driven water splitting has been shown previously [13, 14, 15, 17].

With respect to the performance of the PV-EC device, the majority of literature concerns laboratory tests performed under standard test conditions (STC) [18], e.g. at room temperature and under 1 sun illumination intensity (AM1.5g spectrum). However, an outdoor application of PV-EC devices requires the investigation of device performances under conditions that differ from STC. In this work, we address the influence of the illumination intensity on the performance of an integrated PV-EC device for water splitting. Therefore, we studied the impact of varying the illumination intensity on the performance of a triple junction thin film silicon solar cell. Furthermore, we investigated the performance of an entire integrated device, where two different catalyst systems (Pt/RuO_2 and Ni/Co_3O_4) in combination with the multijunction cells were compared. Platinum and ruthenium oxide provide high catalytic activities towards the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), respectively, but they are rather scarce [19]. More abundant alternatives, such as Ni (HER) and Co_3O_4 (OER), can be used only in alkaline electrolytes and usually show higher overpotentials. While under 1 sun light intensity the operation current in the PV-EC devices substantially differed between Pt/RuO_2 and Ni/Co_3O_4 systems, the difference tends to decrease with decreasing illumination intensity. The origin of this effect is addressed in the paper.

2. Experimental details

All thin film silicon layers were deposited in superstrate configuration by plasma enhanced chemical vapor deposition in a multi chamber system. For the intrinsic absorber layers a mixture of silane (SiH_4) and hydrogen (H_2) gases was used. For the n- and p-type layers, trimethylborane (TMB), methane (CH_4), phosphine (PH_3), and carbon dioxide (CO_2) gases were added to the silane–hydrogen mixture. For microcrystalline silicon (μc-Si:H) intrinsic and p-type layer depositions an excitation frequency of 94.7 MHz was applied. For all amorphous silicon (a-Si:H) layers an excitation frequency of 13.56 MHz was applied. Triple junction (a-Si:H/a-Si:H/μc-Si:H) solar cells were prepared in superstrate configuration. For the intrinsic μc-Si:H absorber layer a silane concentration (SC) of 5.0%, defined as the ratio between the SiH_4 flow and the total gas flow, and a substrate deposition temperature of 180°C was chosen. The intrinsic a-Si:H top and middle sub-cell absorber layers were deposited at 130°C with a SC of 4% and at 180°C with a SC of 10%, respectively. Low refractive index microcrystalline silicon oxide (μc-SiO_x:H) layers [20] were implemented between sub-cells as intermediate reflecting layers to maintained appropriate current matching conditions. The solar cells were deposited on 10×10 cm^2 textured aluminum-doped zinc oxide (ZnO:Al) coated glass substrates (front contact) [21]. Additional details on the solar cell preparation can be found elsewhere [13]. A schematic drawing of the PV-EC device set-up is depicted in Fig. 1.

For the *j-V* characteristics under various light intensity conditions, a class A double source Air-Mass (AM) 1.5 solar simulator (WACOM-WXS-140S-Super) at standard test conditions (AM1.5G, 100 mW/cm^2, 25°C) was used. Different shading filter masks, allowing to maintain the illumination intensities of 0.64, 0.36 and 0.15 sun, were mounted in the optical path to evaluate the device performance under variable incident light intensity.

The utilized approach to calculate the photoelectrochemical performance for integrated devices in combination with different catalytic materials was previously described elsewhere [22, 23].

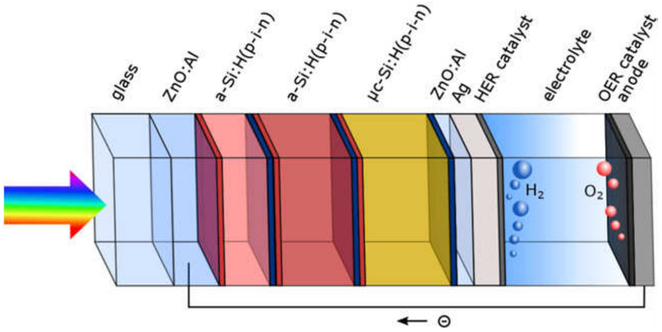

Fig. 1 Schematic drawing of an integrated PV-EC water splitting device set-up featuring a triple junction silicon solar cell in direct contact to an electrolysis cell.

3. Results and discussions

The effect of an illumination intensity reduction on the current–voltage characteristic of the a-Si:H/a-Si:H/μc-Si:H triple junction solar cell is shown in Fig. 2. As expected, the short circuit current density (j_{sc}) decreases with decreasing illumination intensity and the open circuit voltage (V_{oc}) is reduced by around 200 mV in the investigated range of light intensities. The fill factor (*FF*) changes slightly, tending to increase with decreasing intensity. The *FF* of 69.5% in case of 1 sun intensity increases up to 71.9% for the illumination intensity of 0.15 suns. It was previously reported for a-Si:H single junction solar cells [24] and multijunction devices [25], [26] that a reduction in illumination intensity below 1 sun can increase the *FF* value. This effect is generally attributed to an improvement in the built-in field and reduced recombination of photogenerated carriers in the absorber layer. Additionally, the effects of the intensity dependence on the quantum efficiency [27] and consequent influence on the current matching

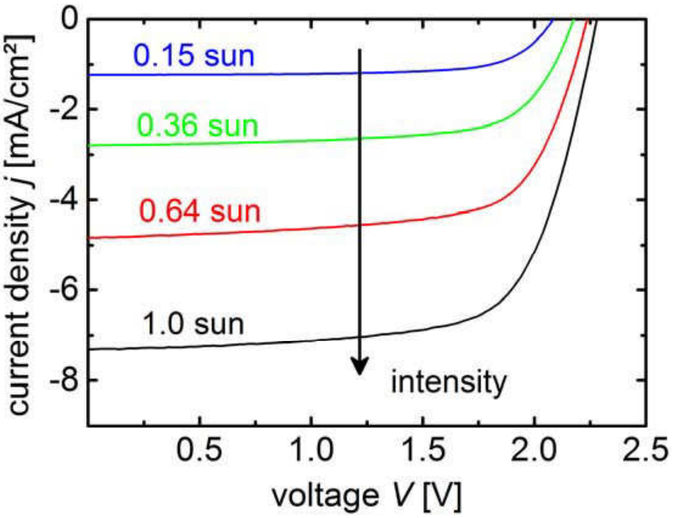

Fig. 2 *j-V* curves measured for a triple junction solar cell under different illumination intensities.

conditions [28] may also contribute to the changes in the fill factor observed here. In the case of thin film silicon single junction solar cells, the open circuit voltage values are typically reduced by around 80 mV per order of magnitude in illumination intensity [24, 25, 26, 29]. This quantitatively agrees well with the reduction in V_{oc} by around 200 mV observed here in the case of a triple junction solar cell and 0.15 suns illumination.

In the following, the experimental data shown in Fig. 2 were used to evaluate the performance of a PV-EC device subject to changes in the illumination intensity, using a semi-empirical model [22, 23, 30]. The corresponding calculated *j-V* characteristics are shown in Fig. 3. The measured *j-V* curves of the triple junction solar cells were combined with the *j-V* curves of the catalysts assuming a behavior according to the Butler-Vollmer equation. As the electrolyte a 1 M potassium hydroxide solution was assumed. The corresponding current–voltage characteristics of the integrated PV-EC device are shown in Fig. 3 for Pt/RuO_2 and Ni/Co_3O_4 catalysts. In the case of a 1 sun illumination intensity, a poorer fill factor of the *j–V* curve featuring Ni/Co_3O_4 catalysts is observed, resulting in a substantially higher operation current j_{op} (the current density at 0V bias) of the PV-EC device utilizing Pt/RuO_2, which is mainly caused by reduced overpotential losses for the Pt/RuO_2 system. Note that, in the case of 1 sun illumination intensity the operation photocurrent density j_{op} of the PV–EC device with Pt/RuO_2 catalysts is located in a relatively flat region of the *j–V* curve, while in the case of Ni/Co_3O_4 catalysts it is located closer to the maximum power point of the photocathode. As a consequence, Ni/Co_3O_4 catalysts result in lower operation current j_{op}.

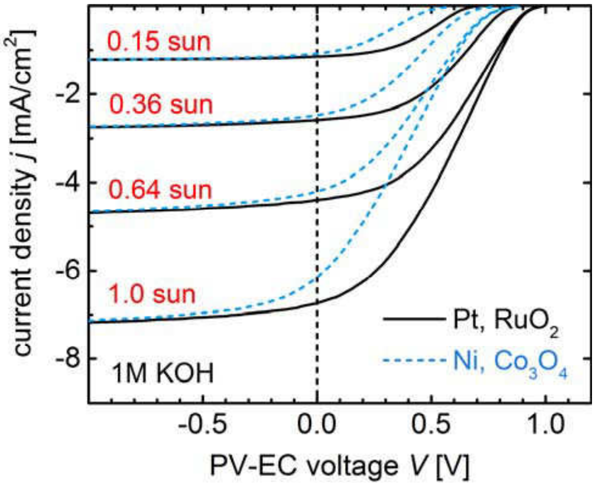

Fig. 3 *j-V* characteristics of a PV-EC device utilizing two different catalyst systems. The *j-V* curves are calculated using a semi-empirical model following the description in refs. [22, 23].

It is evident that a reduction in the light intensity tends to shift the photocurrent plateau region towards higher voltages. For instance, in the case of 0.15 sun intensity j_{op} of both Pt/RuO_2 and Ni/Co_3O_4 are located at a plateau region of the *j-V* curves, as expected from changes in *FF* values discussed above. Therefore in the case of low illumination intensity, no substantial differences in the j_{op} for both catalytic systems can be observed. Reducing the illumination intensity has a smaller impact on the operation current density utilizing the Ni/Co3O4 system, since the slope of the curve is lower than for the Pt/RuO2 system. This effect is shown in Fig. 4 which plots j_{op} vs. the light intensity for both systems.

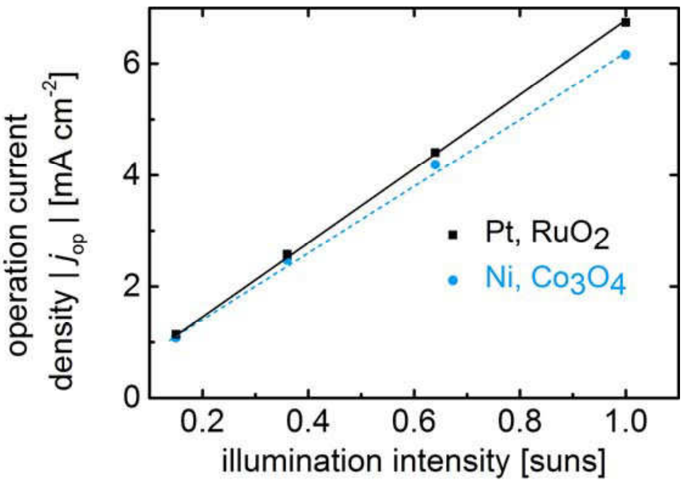

Fig. 4 Impact of the illumination intensity on the operation current j_{op} for both catalytic systems.

4. Summary

We studied the effects of the illumination intensity on the performance of an integrated photovoltaic-biased electrochemical (PV-EC) device for solar hydrogen production. In the case of a triple junction solar cell a reduction in illumination intensity down to 0.15 suns results in a decrease in V_{oc} by around 200 mV. Still, the voltage is sufficient for spontaneous water splitting. Evaluation of systems with very high (Pt/RuO$_2$) and less high (Ni/Co$_3$O$_4$) catalytic activity indicate significant differences in the operation photocurrent of PV-EC device under one sun. This difference tends to reduce with decreasing intensity, which could originate from a slight improvement in the fill factor values of the triple junction solar cell at lower illumination intensities.

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