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Stability and Degradation Mechanism of Si-based Photocathodes for Water Splitting with Ultrathin TiO₂ Protection Layer

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Abstract: Using transmission and scanning electron microscopy, we study mechanisms which determine the stability of Silicon photocathodes for solar driven water splitting. Such tandem or triple devices can show a promising stability as photocathodes if the semiconductor surface is protected by an ultrathin TiO₂ protection layer. Using atomic layer deposition (ALD) with Cl-precursors, 4–7 nm thick TiO₂ layers can be grown with high structural perfection. The layer can be electrochemically covered by Pt nanoparticles serving as electro-catalysts. However, Cl-remnants which are typically present in such layers due to incomplete oxidation, are the origin of an electrochemical degradation process. After 1 h AM1.5G illumination in alkaline media, circular shaped corrosion craters appear in the topmost Si layer, although the TiO₂ layer is intact in most parts of the crater. The crater development is stopped at local inhomogenities with a higher Pt coverage. The observations suggests that reduced Titanium species due to Cl[−]/O^{2−} substitution are nucleation sites of the initial corrosion steps due to enhanced solubility of reduced Ti in the electrolyte. This process is followed by electrochemical dissolution of Si, after direct contact between the electrolyte and the top Si layer

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surface. To increase the stability of TiO_2 protected photocathodes, formation of reduced Ti species must be avoided.

Keywords: electrochemical corrosion; photo-cathode; photoelectrochemical water splitting; Si tandem cells; TiO_2 protection layer.

1 Introduction

High efficiency photo-electrochemical devices for solar-driven hydrogen generation require the integration of different materials, which show optimal performance for the specific functions. Such integrated devices are developed with the goal to establish a higher efficiency in water splitting than modular photovoltaic and electrolysis systems, due to reduced contacts losses [1]. Silicon solar cells are well suited for efficient absorption of the solar spectrum with resulting high conversion efficiencies but require a multi-junction or series connection set-up to provide sufficient voltage for water splitting. However Si and also most other interesting absorbers are not electrochemically stable in aqueous electrolytes [2]. Since most earth abundant efficient oxygen evolution catalysts operate only stable in alkaline conditions, the hydrogen evolution has to be preferably carried out in alkaline electrolyte media, too. Thus, the photocathodes and anodes would be in contact with aqueous alkaline electrolytes so an electrically conducting anticorrosion layer covering the semiconductor absorber in addition to a suitable catalyst is generally needed. Several metal and oxide protection layers have been explored including Pd, Ni, SiO_x , NiO_x and TiO_2 [3–7]. For TiO_2 a durability of >500 h in alkaline conditions has been achieved [8]. Furthermore, it possesses a relatively good electric conductivity and methods for the growth of ultra-thin layers, such as atomic layer deposition (ALD), are established [8–10]. ALD offers the opportunity of deposition of high quality thin films by a layer by layer growth mode, which is required to obtain a fully covered ultrathin film. TiO_2 protection layers of various thicknesses are well established for water splitting devices [6, 8, 10–16], including the combination of a TiO_2 layer with nanostructured TiO_2 for obtaining high surface areas [11]. Generally, there are competing performance requirements on the protection layer. Stability typically improves with increasing layer thickness, however, the photoelectric current density drops because of the higher series resistance. Consequently, ultra-thin conducting layers are highly desirable due to their good charge transport properties, but posing the challenges for layer perfection and thus require a fundamental understanding of the role of defects for corrosion.

In this work we analyze the influence of growth-induced defects and impurities in ultrathin TiO_2 protection layers on the stability and efficiency of a photocathode device. The 4–6 nm thick amorphous TiO_2 protection layer is deposited by ALD on silicon based tandem and triple junctions. The devices are operated for 1 h under AM1.5G in alkaline media (0.1 M KOH) to analyze their stability and processes initiating corrosion. After operation the devices are studied by scanning (SEM) and transmission electron microscopy (TEM). Our results suggest that impurity-induced reduced TiO_2 sites are the origin of an accelerated electrochemical corrosion process.

2 Results

2.1 Pristine state of the photocathode

The pristine photocathodes with Si-based tandem/triple cell, covered with 100x cycles of ALD grown TiO_2 and electrochemically deposited Pt nanoparticles were analysed by SEM and TEM. The TiO_2 and Pt particle features described in the following, do not depend on the Si cell configuration. Exemplarily, the results are summarized in Figure 1 for the tandem cell configuration. Although areas with higher and lower Pt coverage are found (Figure 1c and d, respectively), the TiO_2 film appears in SEM as a homogeneous and smooth layer without any growth features such as e.g. pinholes. This indicates a full TiO_2 coverage in the pristine state. TEM cross-section lamellas are prepared at different photocathodes and different locations. The bright field image (Figure 1b) reveals the expected structure of the photocathode, where even the a-Si/a-Si interface is visible. The junction between the Si sub-cells consists of a thin doped microcrystalline silicon or doped microcrystalline silicon oxide layer, depending on the junction configuration, which is visible in bright field (Figure 1b). The TiO_2 layer is visible in the TEM overview image only at positions without overlap to Pt particles. The bright field image at higher magnification in Figure 1e shows the typical morphology of TiO_2 layer. The film thickness varies between different photocathode samples and is in the range between 4 and 7 nm, fluctuating across the layer by ± 1 nm. The amorphous structure of the TiO_2 layer is confirmed by HRTEM and electron diffraction.

The inhomogeneous coverage of the photocathode by Pt nanoparticles in the pristine state seems to be correlated to the TiO_2 layer thickness. Areas with high Pt density (H.Pt) occur at thicker TiO_2 regions and areas with low Pt density (L.Pt) occur at thinner TiO_2 regions, respectively. Within the sample series the absolute values for Pt density and particle size varies slightly (see ESI S5) but Pt rich and reduced areas are observed for all studied surfaces.

Fig. 1: Configuration of the photo-electrochemical device: (a) Scheme of the device; (b) TEM bright field image in cross section of a tandem cell photocathode; (c) representative SEM image of a photocathode surface at an area with high Pt coverage; (d) area with low Pt coverage; (e) Cross-section TEM bright field image of the TiO_2 layer from an area with high Pt coverage.

2.2 Performance

The photoelectrochemical performances of the tandem and triple cell devices were tested in 0.1 M KOH under AM1.5G illumination by using chronopotentiometry with a constant current density of -2 mA cm^{-2} for 1 h. The corresponding results are depicted in Figure 2.

Both devices show a constant potential at the beginning with initial values of 1.4 V vs. RHE for the tandem cell and 1.8 V vs. RHE for the triple cell. In previous studies, operating times of 12 h could be achieved for similar systems [17]. However, in these studies a titanium dioxide layer thickness of 30.5 nm was used, which is much higher than in the systems reported here. Figure 2 shows that both

Fig. 2: Chronopotentiometry measurement of a tandem and triple cell devices under AM1.5G illumination with a constant current density of -2 mA cm^{-2} for 1 h.

the tandem as well as the triple junction photocathodes experience a decrease of the potential, which is most pronounced for the triple cell device at the end of the measurement. From this observation, an early onset of a continuous device degradation can be concluded, which later turns into a rapid corrosion. The degradation mechanism including the influence of the Pt particle distribution, impurities as well as the passivation layer thickness will be discussed below.

2.3 Post-mortem studies of the photocathode stability

2.3.1 Change in Surface Morphology by SEM

The SEM studies address two topics: (i) The stability of the coverage, shape and size of the Pt nanoparticles and (ii) of the TiO_2 protection layer after 2 h, 4 h, and 6 h of AM1.5G illumination in 0.1 M KOH at -2 mA/cm^2 . For the Pt particle coverage, size distribution and morphology, no significant changes could be observed even after 6 h of hydrogen evolution (ESI S1 & S3). However, in areas with low Pt coverage the formation of circular holes in the TiO_2 layer and the underlying Si film is visible in Figure 3. These circular holes are already present at the surface of the photocathode after 1 h of electrolysis in 0.1 M KOH. In contrast to the hole formation in areas with low Pt coverage, no hole formation can be observed in areas with high Pt density. Remarkably, the lateral hole growth even stops at areas with high Pt coverage (Figure 3a).

Fig. 3: SEM images of the post mortem state of the tandem photocathode after 1 h of operation. (a) detailed view of the corrosion craters at the interface of high and low Pt coverage; (b) Overview of the different areas of high and low Pt coverage. The round shapes in the L.Pt areas are corrosion craters.

The circular shape of the craters indicates, that the hole growth is nucleated at very local point like nucleation centers in the TiO_2 layer and then grows in a concentric manner. The dependence of the crater formation on the Pt nanoparticle coverage provides strong evidence for an electrochemical degradation process of the TiO_2 layer nucleating at defects and a subsequent electrochemical dissolution process of the Si material below the TiO_2 layer. Clearly, hole growth is stopped after reaching an area with high Pt coverage. Consequently a high Pt coverage prevents or at least slows down the electrochemical degradation of the TiO_2 layer and underlying Si. As revealed by the TEM studies of corrosion craters (see e.g. Figure 5), the TiO_2 layer is preserved in most parts of the crater, even at locations where the Si has been dissolved. This supports that the TiO_2 layer is stable under operation conditions and electrochemical corrosion of Si is nucleated at small inhomogeneities and propagates in a concentric manner in low Pt regions.

2.3.2 Post mortem studies of chemical inhomogeneities

In order to further investigate the role of chemical inhomogeneity for the device stability, EDX measurements were carried out. Several EDX spectra were taken in areas with high and low Pt density. These spectra then were summed up accordingly, the background was removed and the signal normalized to the $\text{K}\alpha_1$ Si Reflex. The result in Figure 4 indicates that Cl is present in some areas of the TiO_2 layer. In general, the Cl concentration is the highest in the holes and also in areas with low Pt density compared to the high Pt density areas.

Fig. 4: EDX analysis of the Cl inhomogeneity in corroded and non-corroded areas of a tandem device after 1 h of operation. (a) Overview on EDX spectra at the Cl $K_{\alpha 1}$ line for different areas; (b) SEM images of areas of high (H:Pt) and low (L:Pt) coverage, where coloured circles exemplify areas where the spectra in (a) were taken.

2.3.3 Post mortem TEM studies of the TiO_2 layer and corrosion craters

The cross-section HAADF scanning transmission electron microscopy (STEM) image in Figure 5 displays the edge of a corrosion crater. Within the crater (right side) the Si is only partially removed. The dissolution has stopped at the a-Si/a-Si interface of the solar cell. The EDX maps in Figure 5b and c reveal a partially intact TiO_2 layer within large areas of the holes. This is supported by EDX measurements carried out at a SEM (ESI S4). These findings supports the electrochemical nature

Fig. 5: EDX analysis of a corrosion crater of a tandem photocathode after 1 h of operation in cross plane view; (a) HAADF cross-section image of the edge of the corrosion crater. EDX element maps: (b) Oxygen; (c) Titanium.

of the Si dissolution. Even the Si beneath a preserved TiO_2 layer goes into solution via a lateral process involving neighbouring pin holes. The remaining TiO_2 layers within the craters then just shift down during the Si dissolution, demonstrating the stability of such a protective layer.

Post mortem TEM studies of cross-section lamellas outside the crater regions confirm the results obtained at the pristine devices: Depending on the area, the thickness of the TiO_2 layer varies by a few nanometres (ESI S2). The thickness of the specific photocathode studied has an average value of (7.4 ± 1.2) nm in the area with high Pt coverage and (5.4 ± 0.8) nm in the low Pt density area. Together with the previous results this points toward a correlation between stability, TiO_2 layer thickness, Pt coverage and Cl content. The photocathodes preferably degrade in areas with low Pt coverage, a thinner TiO_2 layer thickness and a higher Cl concentration.

3 Discussion

In the preparation of the TiO_2 protection layer of the photocathode by the ALD process, Ti-tetrachloride is used as the Ti precursor. In addition, K_2PtCl_4 is used for the electrochemical deposition of Pt nanoparticles. The EDX data point toward the ALD process as the origin of the correlation between Cl species and corrosion craters, since no increase in Cl can be detected at or near the Pt particles. Thus, there are Cl impurities stemming from a non ideal ALD process, where Cl-doped $\text{TiO}_{2-x}\text{Cl}_x$ is formed in an incomplete reaction. Such Cl-remnants are typically observed in TiO_2 layer formation by Cl-containing precursors [18, 19].

The calculated Pourbaix diagram as well as cyclic voltammetry studies reveal that TiO_2 is stable at potentials close to HER in alkaline conditions [20, 21]. However, reduced TiO_{2-x} such as the Magneli phase shows a redox peak at -0.1 V vs Hg/HgO [22]. Hence, Ti^{3+} exists in the Magneli phase which is redox active in CV under alkaline conditions. In Cl-doped TiO_2 , Cl is an electron donor, suggesting that Ti^{4+} is reduced due to replacement of O^{2-} by Cl^- . In addition oxygen is more electronegative than Cl, facilitating the formation of reduced Ti^{3+} species in the $\text{TiO}_{2-x}\text{Cl}_x$ layers. The hypothesis that Cl-doping leads to Ti^{3+} formation is additionally supported by the electronic bandstructure calculations of Yang et al, which reveal a shift in the TiO_2 conduction band to lower values due to Cl doping [23]. If Ti^{3+} is already present due to the chemical impurity, it can be even further reduced to Ti^{2+} in the cathodic current branch of the CV.

The Pourbaix diagram [20] suggests that Ti^{3+} and Ti^{2+} is only soluble in the acidic pH regime and TiO_2 transforms into other solid Ti–O phase at potentials negative of the E_0 (HER). However, this applies only in electrochemical equilibrium with an electrolyte containing dissolved Ti species. In our case the Ti

concentration in the electrolyte is basically zero. In non-equilibrium dissolution of Ti^{3+} and Ti^{2+} can set in even in alkaline conditions. The leaching of $\text{Ti}^{3+/2+}$ is consequently facilitated in locally Cl-enriched areas, leading to the formation of small pinholes in the TiO_2 , which can in turn act as nucleation centres for the electrochemical crater formation in Si.

An alternative scenario is the local change of the pH value due to the formation of HCl at the interface of the electrolyte to Cl-doped TiO_2 . This is unlikely because at pH 13 (0.1 M KOH) HCl would immediately react to KCl:

The chemical cathodic etching of Si in alkaline solution is an intensively studied subject due to its importance in Si technology (see e.g. Ref. [24–26]). After extensive studies, the model of a coupled chemical/electrochemical mechanism has been developed which is a combination of an $\text{H}_2\text{O}/\text{OH}^-$ attack of Si–Si or Si–H bonds with the formation of soluble $\text{Si}(\text{OH})_4$ species and anodic currents due to electron injection. Cathodic currents lead to the formation of activated H and Si– H_x bonds which may also form reactive and soluble SiH_x species [27, 28].

The suggested mechanism of crater nucleation by electrochemical dissolution of $\text{Ti}^{3+}/\text{Ti}^{2+}$ at Cl-doped TiO_2 areas and subsequent dissolution of Si (illustrated in Figure 6) is consistent with the following observations: (i) the crater formation depend on the TiO_2 layer thickness. (ii) The crater formation is centred at areas of locally enhanced Cl concentration within the TiO_2 protection layer. (iii) The

Fig. 6: Schematic illustration of the suggested mechanism of pinhole formation in TiO_2 and the subsequent Si dissolution mechanism.

crater formation preferentially takes place at locations of lower Pt particle coverage, where large overpotentials can develop. In addition to Cl-induced preformed Ti^{3+} defect states, a locally increased overpotential can drive Ti^{4+} reduction. The equilibrium potential for Ti^{4+} reduction is -1.38 V compared to -0.82 V for proton reduction in alkaline conditions $\text{pH} = 14$ [29]. (iv) The observation of an intact TiO_2 layer in large areas inside the dissolution craters strongly supports that the TiO_2 can endure HER under alkaline conditions and only the Cl impurities lead to the degradation of the TiO_2 layer. (v) The stop of the vertical degradation of Si at the a-Si/a-Si interface is consistent with the suggested electrochemical degradation mechanism for Si. The removal of one PIN subcell of tandem junction reduces the photovoltage that drives the Si dissolution. (vi) A high Pt coverage can reduce the dissolution of TiO_2 and Si, probably due to a locally reduced overpotential.

4 Conclusion

The degradation of chemical passivation layers on Si photocathodes has been analyzed using TEM and SEM studies. It is evident that the desired HER is competing to other unwanted electron transfer reactions (electron induced Si decomposition). The latter can be suppressed by an ultrathin electrically conductive protection layer which stability is influenced by the layer morphology and stoichiometry. In the case of TiO_2 layers a non-ideal ALD process for the growth of ultrathin TiO_2 layers based on Cl-containing precursors can lead to a Cl doping of the TiO_2 protection layer. As a result locations of partially reduced Titanium represent nucleation centers for the onset of the corrosion. Ti^{3+} dispenses or is further reduced to Ti^{2+} , which can then also dissolve in the electrolyte. To increase the stability of TiO_2 protected photocathodes, defects such as chemical impurities, maybe also oxygen vacancies that give rise to reduced Ti species, must be avoided. The effect of degradation can be reduced by a homogenous coverage of Pt as a co-catalyst. In summary, the chemical composition (impurities) as well as the morphology of the electrochemically involved surface, including the electronically conduction protection layer as well as the catalyst must be well-chosen, for obtaining stable devices.

5 Experimental section

5.1 Preparation of Si-based photocathodes solar cells

Thin-film silicon solar cells were deposited in a p-i-n sequence (superstrate configuration) by a Plasma Enhanced Chemical Vapor Deposition (PECVD)

technique in a multi-chamber system. All solar cell (a-Si:H/a-Si:H tandem and a-Si:H/a-Si:H/ μ c-Si:H triple) were deposited on 100 cm² fluorine-doped tin dioxide (SnO₂:F) coated glass substrates (Asahi U type) at substrate temperatures below 185 °C. For the intrinsic absorber layers (i-layers) a mixture of silane (SiH₄) and hydrogen (H₂) gases was used. For the doped p- and n-type layers, trimethylborane (TMB), methane (CH₄), phosphine (PH₃), and carbon dioxide (CO₂) gases were added to the silane–hydrogen mixture. For μ c-Si:H intrinsic and p-type layer depositions an excitation frequency of 94.7 MHz was used. For all a-Si:H layers an excitation frequency of 13.56 MHz was used. Additional details on the solar cell preparation can be found in refs [30, 31].

5.2 Device integration

The prepared silicon solar cells were coated with thin films of amorphous TiO₂ for surface passivation and corrosion protection by using a custom-built thermal ALD reactor. Titanium tetrachloride (99.995%, Sigma-Aldrich) and Milli-Q water were used as precursors at a growth temperature of 160 °C with high purity nitrogen (99.999%) as a purging gas. Detailed information about the ALD are given in Cottre et al. [17]. Prior to the TiO₂ deposition etching procedures were used for the surface preparation. The a-Si:H/a-Si:H tandem cells were etched with ammonium fluoride (40%, semiconductor grade VLSI PURANAL, Sigma-Aldrich) for 5 min while the a-Si:H/a-Si:H/ μ c-Si:H triple cells were cleaned by using a piranha bath with sulfuric acid (96%, VLSI Selectipur, BASF) and hydrogen peroxide (31%, VLSi Selectipur, BASF) in a defined ratio (H₂SO₄:H₂O₂ = 3:1) for 5 min. The next step of the device integration is the preparation of the Pt electrocatalyst particles for the hydrogen evolution reaction by galvanostatic electrodeposition. Unless otherwise stated 2 mM K₂PtCl₄ (99%, Carbolution Chemicals GmbH) in 0.5 M H₂SO₄ ($\pm 0.2\%$, Carl Roth GmbH) solution was used. The Pt deposition was carried out with a current density of -0.5 mA cm^{-2} for 120 s in a three-electrode setup under AM1.5G illumination with a silver/silverchloride (3 M NaCl) reference electrode and a platinum wire as a counter electrode.

5.3 Photoelectrochemical characterization

The photoelectrochemical characterization of the integrated systems was performed in a three electrode setup in 0.1 M KOH ($\pm 0.2\%$, Carl Roth GmbH) under AM1.5G illumination. The formation of an ohmic contact to the TCO was achieved by scratching the silicon solar cells and using colloidal silver paste (Ted Pella Inc). The photoelectrochemical measurements were performed in a Zahner PECC-2 cell with a Gamry potentiostat (Interface 1000). The reference electrode was a

silver/silverchloride electrode (3 M NaCl) while a platinum wire was used as a counter electrode. The spectral light incidence (AM1.5G) was created by a full spectrum solar simulator equipped with a 150 W Xe short arc lamp (LS0108, LOT-QuantumDesign GmbH). The integrated devices were also tested in a two electrode setup under AM1.5G illumination in a modified Zahner PECC-2 cell combined with a commercial ruthenium-iridium oxide counter electrode (Metakem GmbH) for the oxygen evolution reaction. Here various electrolyte solutions were used (0.1 M and 1 M KOH ($\pm 0.2\%$, Carl Roth GmbH) and 0.1 M and 1 M H₂SO₄ ($\pm 0.2\%$, Carl Roth GmbH)) to study the performance of the systems in dependence of the pH value. The respective photoelectrochemical measurements of the two electrode setup can be found in Cottre et al. [17].

5.4 SEM and EDX

The SEM analysis was carried out with a Nova NanoSem 650 *in-situ* SEM from FEI. An Everhart-Thornley (ET) detector was used to take overview images while the more detailed images were taken with a “through the lens” (TTL) detector. In every case an acceleration voltage of 10 kV was used.

For energy-dispersive X-ray spectroscopy (EDX) an acceleration voltage of 20 kV was used and an Oxford Instrument X-Max detector was employed. The livetime for each spectrum was 120 s and a minimum of 10 spectra per specific area was used for the analysis.

In the case of the cross-section lamella EDX analysis in Figure 5 the SEM was operated in scanning transmission electron microscopy (STEM) mode where for imaging a High Angle Annular Dark Field (HAADF) detector was deployed.

5.5 TEM lamellae preparation and TEM analysis

Cross-section TEM lamellas were cut using a Nova Nanolab 600 focused ion beam (FIB) system from FEI with an ion acceleration voltage of 30 kV.

First a protective layer of FIB-Platinum was deposited via electron beam induced deposition. Then a thicker layer was fabricated by ion beam induced deposition. After rough cuts with 7 nA and 3 nA currents a transfer to a copper grid was performed and cleaning cuts with down to 29 pA at 5 kV were carried out.

The TEM investigations were performed with a Phillips CM12 at 120 kV (overview image in Figure 1b). The TiO₂ layer thickness was measured with a Phillips CM 30 at 300 kV (Figure 1e and Figure S2).

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