Supplementary Information

MoS$_2$—an integrated protective and active layer on n$^+$p-Si for solar H$_2$ evolution

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Contents

Experimental section ........................................................................................................................................ 2
  Electrode preparation ................................................................................................................................. 2
  Electrochemical testing .............................................................................................................................. 3
  MoS$_x$ catalyst deposition ......................................................................................................................... 4
  Deposition of Pt ......................................................................................................................................... 4
  X-ray photon spectroscopy (XPS) measurements .................................................................................... 5

Supplementary data ................................................................................................................................ 5
  MoS$_x$ depositions .................................................................................................................................. 5
  Tafel analysis ........................................................................................................................................... 7
  XPS characterization of MoS$_2$/Mo/n$^+$p-Si electrodes ....................................................................... 7
  XPS characterization of WS$_2$/W/n$^+$p-Si electrodes ........................................................................... 14
  UV/Vis analysis of surface coatings: ...................................................................................................... 16

References .................................................................................................................................................. 18
Experimental section
Electrode preparation
Single-crystal B-doped (p-type, (100) oriented) 100 mm diameter silicon wafers (0.5 mm thick, 2.2 Ω cm resistivity) were obtained from Okmetic. To achieve a Si wafer design similar to that of the Lewis group\textsuperscript{1}, the wafers were doped with phosphorous by a vapor phase surface doping process in an atmospheric pressure tube furnace using POCl\textsubscript{3} as the P source. The surface doping was carried out at 900°C for 10 minutes whereby a shallow n+p-junction is formed in the surface of the p-type wafer. Using UV photolithography and a 3 μm deep part of the n\textsuperscript{+}p-Si was etched away, by reactive ion etching, to form 10 mm diameter circular n\textsuperscript{+}p-junction area. Using UV photolithography the wafers were patterned with a lift-off mask that would allow deposition on the circular junction areas only. The samples were then dipped in buffered HF (NH\textsubscript{4}F-HF) to remove the native oxide and hydrogen terminate the surface. Within 10 min the samples were transferred to a vacuum chamber and pumped down to avoid the formation of a surface oxide. Then 10 nm Mo was then sputtered on the n\textsuperscript{+}p-Si mesa using a shadow mask. A profilometer was used to calibrate the Mo sputter rate, which then allowed us to deposit approximately 10 nm. After sputtering the mask was lifted off in an acetone treatment.

The electrodes were then cut to 16 x 20 mm pieces, and sonicated in both ethanol and MilliQ water (18 MΩ) for 15 minutes each to remove any contaminants.

The electrodes were placed in the hot zone of a tube furnace, the quartz tube was evacuated to 10 mTorr and backfilled with Ar three times. Then a flow of approximately 20 mL/min was established over the samples. The furnace vented through a 3.5 m 1/8 inch tube into a 25\% ammonia solution bubbler acting as a scrubber, to eliminate backflow of oxygen. Ground glass connections were sealed with a silicon based high-temperature vacuum grease.

The temperature of the furnace was increased to 450 °C at a ramp rate of 5 K/min and held at temperature for 4 hr, then cooled to room temperature at 5 K/min. After cooling the electrodes were removed from the furnace.

Ga-In eutectic (Aldrich) was then scratched into the back of the silicon wafer. A copper wire was then inserted into the eutectic and the eutectic was then covered in silver paint (SPI Supplies, PA, USA). The copper wire was then inserted into a pyrex glass tube approximately 10 cm long. The back of the electrode was finally covered in a hot melt adhesive (purchased from a local hardware store, Bosch). Which prevented the electrode from being chemically attacked by the electrolyte. For longterm experiments the electrode connection was covered by a Hysol 1C two component epoxy, the epoxy was cured at 50-60 °C for 12 hr in air. The copper wire extending out from the opposing side of the glass tubing was then attached to an alligator clip from the electrochemical system. The electrode was then wrapped in Teflon tape. A circular hole in the Teflon tape corresponding to 5 mm diameter was placed directly over the n+p junction.

This made an active surface area of 0.196 cm\textsuperscript{2}.
Electrochemical testing

Electrodes were tested in a custom-made pyrex H-cell. A luggin with a glass fritt was fitted with a Hg/HgSO₄/K₂SO₄(sat) reference electrode. The electrolyte was 1M HClO₄ (Sigma) in MilliQ water. Electrolytes were purged with H₂ (AGA H₂ instrument purity) for minimum 20 min to remove oxygen before experiments were commenced. All glassware was cleaned in Piranha (1:3 35% H₂O₂/95-98% H₂SO₄(Sigma-Aldrich)) and then sonicated in MilliQ water three times before experiments.

During measurements the electrode surface was illuminated with a 150W Xe lamp solar simulator (Newport) fitted with a red filter (cut off <635 nm), IR water filter, and AM1.5g filter to resemble the red part of the solar spectrum. Light intensity was adjusted to fit the AM1.5g reference spectrum² (39.5mW/cm²). See Fig. S 1.

For long-term experiments a Xe-lamp fitted with a light guide was used, light were shone through a red filter (<635 nm cut-off). As light could not be adjusted to match the AM 1.5g solar spectrum distance was roughly optimized based on obtained limiting photocurrent densities and were then adjusted post experiment by linear scaling so that the photon limited current matched that measured under AM1.5g illumination. Usually light intensity fitted within a factor of approximately two.

Measured electrode potentials were corrected to the reversible hydrogen electrode (RHE) by adding the standard potential for the Hg/HgSO₄ electrode (0.680V vs SHE) and correcting for pH following the equation E=E_{measured} + 0.680V + 0.059V*pH (as all measurements are carried out at pH 0 the pH correction is 0V).

Before performing the Tafel analysis, the measured potential was corrected for the IR-drop resistance and adjusted for photocurrent to give the actual overpotential for the HER. The solution resistance was measured for representative electrodes using Biologic software EIS measurements at potentials between 0.5 and 0 V vs Hg/HgSO₄. Resistances varied between 15-
20 Ω for different samples and applied potential, the lower bound 15 Ω was therefore used for all samples. To correct for the photovoltage the potential of zero current for the Pt/MoS2/Mo/n+p-Si was measured to be +0.508V vs RHE. Because Pt catalyzes the HER reversibly at pH 0 and 1 atm. Of H2 then the difference between the observed onset potential of the cathodic current and 0V vs RHE is equal to the potential applied by the photoelectrode. By subtracting this potential one then corrects for the entire photovoltage exerted by the complete electrode including the MoS2 layer and n+p-junction. The correction was done according to equation: \( E = E_{\text{measured}} + 0.680 \text{ V} - 0.508 \text{ V} + 15\Omega*I \).

**MoSx catalyst deposition**

All chemicals were used as received. All glassware was cleaned in piranha solution then sonicated in MilliQ 18.2 MΩ water four times. MilliQ water was also used for electrolytes.

Deposition solutions were made according to the procedure by the X. Hu group. Before preparation the MilliQ water was purged with argon (AGA Argon 5.0 instrument purity) for minimum 12 hr after mixing with NaClO4 (Sigma-Aldrich). The solution was then stored in an Ar glovebox. Finally, (NH4)2MoS4 (Sigma-Aldrich, reagent purity) was added to make the solution 2 mM. The solution was sonicated at least 10 min before use, and the solution was kept under Ar until used.

The deposition solution was poured into the deposition H-cell under Ar flow to avoid oxygen. An H-cell was equipped with a glass-fritted Luggin capillary fitted with the reference electrode (Hg/HgSO4/K2SO4 (sat.)). The Pt mesh counter electrode compartment was separated from the working electrode by a glass fritt to avoid Pt contamination. During deposition the electrodes were irradiated with the red light (\( \lambda > 635 \text{ nm} \)) from a 150W Xe lamp placed approximately 1 cm from the sample (approx. 39mW/cm²). It should be noted that the deposition solution strongly absorbs visible light, which causes the actual illumination of the photocathode to be less than the 39mW/cm² measured at the electrode’s distance from the lamp in air. All depositions were done using a Biologic VSP potentiostat.

In the method described by X. Hu and co-workers the potential of the electrode is scanned from -0.363 and 0.747 V versus RHE. Due to the irradiation of n+p-Si resulting in a photovoltage of about 0.50 V (see section above) the applied potentials were shifted to 0.137 and 1.247 V versus RHE, thus allowing the electrodeposition to occur. The samples were scanned between these potentials 19 times (see Fig. S 2)

**Deposition of Pt**

The Pt electrode consisted of dropcasting 10 µL of an aqueous 0.5 µg Pt/µL solution of dinitrosulphatoplatinate salt (Johnson-Matthey) on a MoS2/Mo/ n+p-Si electrode. The electrode was initially photoirradiated at a negative potential allowing for reduction of the Pt salt to Pt metal.
X-ray photon spectroscopy (XPS) measurements

Angle Resolved X-Ray Photoelectron Spectroscopy (AR-XPS) measurements were taken on a Theta Probe instrument (Thermo Scientific). The Ultra High Vacuum (UHV) chamber had a base pressure of $5 \times 10^{-10}$ mbar but it was allowed to reach $5 \times 10^{-9}$ mbar due to degasing from the samples (mainly water from the electrolyte). The X-ray source is monochromatized Al $K\alpha$ (1486.7 eV), giving a resolution better than 1.0 eV at the employed pass energy of 100 eV. An X-ray beam size of 400 µm was chosen for all measurements. The analyzer has an acceptance angle of 60°, between 20° and 80° to the surface normal.

Overview XPS spectra were taken before and after testing in order to identify possible contaminations. Subsequently, detailed spectra of the main peaks for each element were acquired for the fitting and quantification. The peak intensities were integrated after subtraction of a Shirley-type background and corrected for the transmission function of the analyzer, estimated mean free path values and Scofield cross sections. The Mo 3d-S 2s, the S 2p and the Si 2p regions of the spectra were fitted with a convolution of a Gaussian and a Lorentzian functions in the weighted ratio of 20% to 80%, which was found to give the best results. For the quantification of the S signal, the S 2p peak was preferred since the S 2s overlaps with the Mo 3d peaks and thus gives rise to a questionable precision, the S 2p peak on the other hand gave a clear Mo to S ratio consistent with a MoS$_2$ phase.

For the depth profile, an Ar$^+$ ion beam of 1 µA (accelerating voltage of 1 kV) was rastered over a 4 x 4 mm area of the sample. 30 cycles of 60 seconds long sputtering were alternated to detailed XPS measurements of the O 1s, C 1s, Mo 3d, Si 2p regions.

For the angle resolved profiles, 16 different channels were analyzed in parallel (between 20° and 80° to the surface normal), without tilting the sample: this corresponds to 3.75° wide angle intervals. Angle resolved data were processed using the simulation tool, ARProcess (Thermo Avantage software), which uses a maximum entropy method combined with a genetic algorithm to define the depth profiles: angles over 65° were omitted to minimize the effects of elastic scattering.


Supplementary data

MoS$_x$ depositions

The MoS$_x$ depositions are conducted as described above.
Fig. S 2 shows the deposition of the MoS\textsubscript{x} catalyst on the MoS\textsubscript{2}/Mo/n\textsuperscript{+}p-Si. The four features were equivalent to the ones described in literature for the MoS\textsubscript{x} catalyst. When the catalyst was redeposited after running the HER for 24 hr, the features were slightly changed. The oxidative feature at 0.8 V vs. RHE and the reductive feature at 0.4 V vs. RHE split up into two. The reason for this change is still not understood but was considered beyond the focus of this study. Furthermore, all the features start at a larger current indicating that even if the HER activity had dropped to a value resembling the unmodified MoS\textsubscript{2}/Mo/n+p-Si electrode, the surface was closer to the MoS\textsubscript{x} catalyst than to the initial flat MoS\textsubscript{2} surface. We propose that this could have been due a roughening of the MoS\textsubscript{2} as the MoS\textsubscript{x} was deposited, this roughness did not disappear when the nanoparticulate MoS\textsubscript{x} were slowly removed. This demonstrated the inherent stability of the MoS\textsubscript{2} protective layer and indicated that the interaction between the MoS\textsubscript{2} surface and the MoS\textsubscript{x} might be more advantageous than for other electrode surfaces. When the MoS\textsubscript{x} catalyst was redeposited the second time the new features at 0.3 V and 0.6 V vs RHE were even more pronounced, the peak height was still about the same as for the first redeposition. This demonstrated that the redeposited catalyst was very similar at consecutive depositions, showing that the MoS\textsubscript{2} layer was indeed stable to the redeposition of the MoS\textsubscript{x} catalyst.
Tafel analysis

Fig. S 3 and S 4 show the Tafel analysis of the MoS$_2$/Mo/n$^+$p-Si (red), MoS$_x$/MoS$_2$/Mo/n$^+$p-Si(blue), and Pt/MoS$_2$/Mo/n$^+$p-Si(black). In the figures the linear fit for the Tafel analysis are indicated with red lines. Fig. S 3 shows data corrected for the IR-drop whereas Fig. S 4 shows the non-corrected data.

![Figure S 3 Tafel analysis with IR-drop correction for the MoS$_2$/Mo/n$^+$p-Si (red), MoS$_x$/MoS$_2$/Mo/n$^+$p-Si(blue), and Pt/MoS$_2$/Mo/n$^+$p-Si(black). Scan speed 5 mV/s in 1 M HClO$_4$ under red light AM 1.5g illumination.](image1)

![Figure S 4 Tafel analysis without IR-drop correction for the MoS$_2$/Mo/n$^+$p-Si (red), MoS$_x$/MoS$_2$/Mo/n$^+$p-Si(blue), and Pt/MoS$_2$/Mo/n$^+$p-Si(black). Scan speed 5 mV/s in 1 M HClO$_4$ under red light AM 1.5g illumination.](image2)

Tabl. S 1 below show the results of the Tafel analysis.

*Tabl. S 1 Summary of the Tafel analysis in Fig. S 3 and S 4. Tafel slope for Pt is uncommonly low before IR correction due to the few number of points over which the slope could be averaged, after IR correction a more reliable and higher number is obtained.*

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Tafel Slope ([mV/dec])</th>
<th>Exchange current (J$_o$/[A/cm$^2$])</th>
<th>Tafel Slope ([mV/dec])</th>
<th>Exchange current (J$_o$/[A/cm$^2$])</th>
<th>IR compensation ([Ω])</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$/Mo/n$^+$p-Si</td>
<td>112.23</td>
<td>2.31E-06</td>
<td>103.84</td>
<td>1.69E-06</td>
<td>15</td>
</tr>
<tr>
<td>MoS$_x$/MoS$_2$/Mo/n$^+$p-Si</td>
<td>60.79</td>
<td>1.36E-06</td>
<td>48.76</td>
<td>3.57E-07</td>
<td>15</td>
</tr>
<tr>
<td>Pt/MoS$_2$/Mo/n$^+$p-Si</td>
<td>26.97</td>
<td>6.32E-04</td>
<td>36.04*</td>
<td>0.00135</td>
<td>15</td>
</tr>
</tbody>
</table>

XPS characterization of MoS$_2$/Mo/n$^+$p-Si electrodes

Fig. S 5 show the XPS detail spectra of the Mo 3d and S 2p region from the sputter profile in Fig. 1 at the interface of the Si electrode (after 1020 sec sputtering). The spectra shows that the Si is unoxidized and that there is a small feature attributable to MoO$_2$ at this depth. It is unlikely that this small amount of oxide is due to an oxidation of the metal layer to this depth as the main portion of the Mo is metallic. It seems more likely that this is caused by the sputtering process, so-called forward sputtering of the oxide.
Fig. S 5 (left) Si region and (right) Mo region of the Si interface of the Mo/n+p-Si electrode prior to sulfidation.

Fig. S 6 below is shown the overview spectrum for the as-prepared MoS$_2$/Mo/n$^+$p-Si electrode at 20° (top down). In the spectrum besides the expected Mo, S, and C also O and Si lines were observed. As shown below, because the MoS$_2$ was not oxidized it is unlikely that the O stems from oxidized Mo species. As the Si was shifted to the binding energies of SiO$_2$ it was assumed that these peaks originated from an impurity of SiO$_2$ on the surface. Because the XPS sputterprofile shown in the manuscript before sulfidation show no SiO$_2$ signals it was concluded that the impurity was most likely a small amount of vacuum grease from the tube furnace in which sulfidation was carried out that had gotten onto the surface. As it may be seen in Fig S 6 showing the survey spectrum after 144 hr hydrogen evolution the signal had indeed disappeared indicating that the impurity was removed during operation.
Fig. S 6 XPS survey spectrum of the MoS$_2$/Mo/n$^+$p-Si electrode surface at a surface tilt of 20°.

Fig. S 7 also shows that two new impurities had appeared on the surface. These impurities were Ag, Cu and Cl. The two former must have originated from the electrode contact. This demonstrates the difficulties in preparing samples that can run for extended periods of time without contaminating the electrolyte at the harsh conditions of 1 M HClO$_4$. The impurities were very minor and did not affect the catalytic activity of the sample (see manuscript), they were thus disregarded in the following. The Cl stems from residue of the HClO$_4$ electrolyte.
Fig. S 7 XPS survey spectrum of the MoS$_2$/Mo/n$^+$p-Si electrode surface, after running 144 hr hydrogen evolution, at a surface tilt of 20°.

Fig. S 8 and Fig. S 9 show the detail spectra of the binding energy region where the Mo3d and S2s peaks appeared and the region of S2p. The fitted peaks showed three binding energies of Mo, and 1 for S. The Mo3d$_{5/2}$ binding energies of 227.8 eV, 228.8 eV, and 232.6 eV were indicative of Mo, MoS$_2$, and MoO$_3$, respectively. This shows that the MoS$_2$ layer had formed some surface MoO$_3$, which was verified by the ARS-XPS vide infra. The MoO$_3$ content was only approximately 1.6% making this a minor impurity. The presence of the Mo layer was a clear indication that the sulfidation had not penetrated the metallic layer deposited on the Si, this means that fully optimizing the thickness of the Mo layer deposited could increase the light absorption in the Si by decreasing the loss due to reflection by the intermediate metallic layer. When fitted the ratio of S/Mo are 1.4 (S2s/Mo3d) and 2.1 (S2p/Mo3d), respectively. The discrepancy was due to the intrinsic measurement uncertainty and changed slightly when other literature sensitivity factors were used, see the section on XPS measurements above. It was thus concluded that the composition of the MoS$_2$ layer was very close to the stoichiometric ratio of 2.
Fig. S 10 and Fig. S 11 shows the detail spectra of the Mo3d and S2s and S2p regions after 144 hr of hydrogen evolution, it was clearly seen that the spectra changed little upon extended reaction. It was further observed that the S/Mo was still 1.3 (S2s/Mo3d) and 2.0 (S2p/Mo3d) indicating that S did not leach during reaction and the protection layer was indeed stable throughout extended reaction periods.

Fig. S 12 shows the ARS-XPS profile of the as-made MoS2/Mo/n+p-Si with the aforementioned impurities included. The Si signal was seen to be a surface species only and it could therefore be ruled out that it was due to pinholes in the MoS2 layer exposing the substrate Si electrode. Furthermore, the MoO3 signal was seen to be a surface species too, indicating that it was due to a slight surface oxidation of the MoS2 likely caused by air-exposure. Because the oxide signal was less than 2 at.% this surface oxide would not cause a substantial degradation of the protection.
layer even if the electrode was to be repeatedly exposed to air, likely due to its self-limiting nature.

Fig. S 13 shows the ARS-XPS profile after running the HER for 144 hr. It was observed that the previous SiO₂ contamination had disappeared. It may also be seen that the Cu and Ag impurities were surface impurities most likely originating from leaching of the electrode contact, even when this was covered in epoxy. This illustrates the need for highly stable epoxies in an eventual application or the need for contact free PEC designs. It is beyond the scope of this work to avoid these impurities, we will just note that it had no net effect on the HER activity.

From these analyses it was concluded that the MoS₂/Mo/n⁺p-Si was stable under the employed conditions for performing the photoelectrocatalytic hydrogen evolution for at least 6 days with no change in surface structure or loss of activity, which is a prerequisite for industrial application.
Table S 2 show the summary of the XPS fits before and after testing for 144 hr.

<table>
<thead>
<tr>
<th>Element (Chemical state)</th>
<th>Peak name</th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$E_B$ (eV)</td>
<td>S/Mo</td>
</tr>
<tr>
<td>$S$ ($\text{MoS}_2$)</td>
<td>S 2p $3/2$</td>
<td>161.7</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>S 2p $1/2$</td>
<td>162.9</td>
<td>163.0</td>
</tr>
<tr>
<td>$S$ ($\text{MoS}_2$)</td>
<td>S 2s</td>
<td>226.0</td>
<td>1.4$^a$</td>
</tr>
<tr>
<td>$\text{Mo (Mo)}$</td>
<td>Mo 3d $5/2$</td>
<td>227.8</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>Mo 3d $3/2$</td>
<td>230.9</td>
<td>230.9</td>
</tr>
<tr>
<td>$\text{Mo (MoS}_3$</td>
<td>Mo 3d $5/2$</td>
<td>228.8</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>Mo 3d $3/2$</td>
<td>232.0</td>
<td>232.0</td>
</tr>
<tr>
<td>$\text{Mo (MoO}_3$</td>
<td>Mo 3d $5/2$</td>
<td>232.6</td>
<td>NA</td>
</tr>
</tbody>
</table>

$^a$ quantified separately without S2p quantification.

Fig. S 13 ARS-XPS depth profile for a MoS$_2$/Mo/n+p-Si electrode after 144 hr of HER.
XPS characterization of WS$_2$/W/n$^+$p-Si electrodes

Fig. S 14 shows the ARS-XPS depth profiles of the WS$_2$/W/n$^+$p-Si electrode after sulfidation. From the profile and detail spectra (Fig. S 15-17) it was determined that a surface oxide (W3d$_{5/2}$ 35.5 eV, W3d$_{3/2}$ 37.8 eV, and O 1s 532.1 eV) had formed on top of the WS$_2$ (W3d$_{5/2}$ 32.1 eV & W3d$_{3/2}$ 34.3 eV and S2p$_{3/2}$ 161.8 eV & S2p$_{1/2}$ 163 eV) film similarly to the MoS$_2$/Mo/n$^+$p-Si (see Fig. S 12). In addition to this surface oxide—likely formed due to air exposure—a subsurface oxide was observed between the WS$_2$ and the W metal (W3d$_{5/2}$ 31.2 eV and W3d$_{3/2}$ 33.2 eV). This subsurface oxide (W3d$_{5/2}$ 35.5 eV and W3d$_{3/2}$ 37.8 eV) was most likely also WO$_3$, based on the binding energy even if the atomic ratio of oxygen to W indicated a lower oxidation state. It was not possible to fit a significant peak at the binding energy of WO$_2$, so the discrepancy was attributed to an inaccurate fit of the W and O peaks due to overlap with neighboring peaks.

In addition to the WO$_3$, WS$_2$, and W signals C, O, and Si signals were observed just as for the MoS$_2$/Mo/n$^+$p-Si electrodes, these impurities was ascribed to carbon from the air exposure and SiO$_2$ was due to small residues from the vacuum grease used to seal the oven. In addition to these impurities a small signal attributed to Pb was detected but could not be explained.
Fig. S 14 ARS-XPS depth profile for a WS$_2$/W/n'p-Si electrode after H$_2$S treatment. (Top) only the major components (bottom) depth profile for all observed elements.

Fig. S 15-17 shows the overview spectrum, and the detail spectra of S2s, S2p, and W3d. The quantification based on the fitted detail spectra is given in Table S 3.

Fig. S 15 XPS analysis of the W 3d region. Spectrum is fitted with 3 doublet Gaussians for the 3 W phases. A Shirley background is included.

Fig. S 16 XPS analysis of the S 2p region. Spectrum is fitted with 1 doublet Gaussians for the WS$_2$ phase. A Shirley background is included.
**Table S 3 Summary of the XPS fits of the spectra in Fig. S 14-16.**

<table>
<thead>
<tr>
<th>Element (Chemical state)</th>
<th>Peak name</th>
<th>( E_B ) (eV)</th>
<th>S/W</th>
<th>Atomic conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>S (WS(_2))</td>
<td>S 2p (_{3/2})</td>
<td>161.8</td>
<td>2.7</td>
<td>55.0%</td>
</tr>
<tr>
<td></td>
<td>S 2p (_{1/2})</td>
<td>163.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W (W)</td>
<td>W 3d (_{5/2})</td>
<td>31.2</td>
<td>NA</td>
<td>4.5%</td>
</tr>
<tr>
<td></td>
<td>W 3d (_{3/2})</td>
<td>33.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W (WS(_2))</td>
<td>W 3d (_{5/2})</td>
<td>32.1</td>
<td>2.7</td>
<td>20.2%</td>
</tr>
<tr>
<td></td>
<td>W 3d (_{3/2})</td>
<td>34.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W (WO(_3))</td>
<td>W 3d (_{5/2})</td>
<td>35.5</td>
<td>2.0(O/W)</td>
<td>6.8%</td>
</tr>
<tr>
<td></td>
<td>W 3d (_{5/2})</td>
<td>37.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O (WO(_3))</td>
<td>O 1s</td>
<td>530.4</td>
<td>2.0(O/W)</td>
<td>13.5%</td>
</tr>
</tbody>
</table>

**UV/Vis analysis of surface coatings**

To evaluate the effect of metal protection layer and subsequent sulfidation on effective illumination of the n’p-Si the same thickness of metal was sputtered onto quartz wafers. Pieces of this wafer were then measured in a UV/Vis spectrometer between 400 and 800 nm. The resulting absorption profiles are shown in Fig. S 18.
Fig. S 18 UV/Vis absorption of a quartz wafer with (from the top) 10 nm W, 10 nm Mo after sulfidization, 10 nm Mo, and 10 nm W sulfidization.

From the trace of MoS\textsubscript{2}/Mo (red) it may be seen that in the illumination region 630-800nm the surface layer of MoS\textsubscript{2}/Mo transmits on average 33.4\% of the light. Accounting for the absorption in the illumination spectrum, the IPCE limiting current become -9.2mA/cm\textsuperscript{2}, this is quite a bit lower than the observed -12mA/cm\textsuperscript{2} limiting photocurrent for the MoS\textsubscript{2}/Mo/n\textsuperscript{+}p-Si sample. The discrepancy may be attributed to the experimental uncertainty in the thickness of samples due to variations in exact thickness of the metal layer, surface oxidation upon air exposure (this could determine the sulfidization depth as MoO\textsubscript{3} is easier to convert to MoS\textsubscript{2} than Mo\textsuperscript{5,6}) and to a lesser extent the exact positioning of the electrode. It should be noted that the adhesion of W was poor on the quartz compared to the H-terminated Si which could cause pin-holes in the WS\textsubscript{2}/W layer and thus an unrealistic high transmission.

The difference between the Mo layer and the MoS\textsubscript{2}/Mo layer shows that upon sulfidization the absorption of the surface layer increases. This is likely due to the conversion of visible light transparent MoO\textsubscript{3} into MoS\textsubscript{2} which has a band gap of 1.7 eV (or 719 nm). This conversion is also seen as weak features (red trace) in the otherwise fairly linear absorption background of Mo (green trace). This indicates that the limiting photocurrent would be increased by tailoring the thickness of the residual Mo layer without increasing the MoS\textsubscript{2} layer thickness further.
In addition, the absorption of WS$_2$/W suggests that the slightly more positive OCP for the Pt/WS$_2$/W/n$^+$p-Si sample could be due to absorption in WS$_2$ as indicated by the appearance of an absorption band at 700 nm in the WS$_2$/W layer. This indicates that the WS$_2$ is capable of absorbing some amount of light whereas the MoS$_2$/Mo layer does not show an absorption edge and therefore is not expected to contribute to the photovoltage.

**Effect of MoS$_2$ surface roughening**

Using Fresnel’s equation assuming a perpendicular illumination on a planar Si photoelectrode in water one can calculate the maximal reflection and thus the improvement possible in the case of a perfect anti-reflectance coating:

$$\text{Reflectance} = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2 = \left(\frac{3.96 - 1.33}{3.96 + 1.33}\right)^2 = 0.25$$

Where $n_1$ and $n_2$ is the refractive index of Si and water, respectively. This demonstrates the theoretical maximal improvement one may achieve based on the decrease of the surface reflectance. As MoS$_2$ has an average refractive index of 6.27 (450–700nm) the possible improvement at the water MoS$_2$ interface is potentially as high as 0.42 or 42%. This gives the order of magnitude improvement likely causing the increased limiting photocurrent density in Fig. 4, which is in reasonable agreement with the improvement.

**References**


2. NREL, *AM 1.5g solar spectrum*, 2012.


